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The Use of Secondary Condensates from Evaporation Plant in Pulp Bleaching

Master´s thesis for the degree of Master of Science in technology,

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ABSTRACT

High water consumption is a key concern in pulping industry. To resolve the issue, secondary condensates from evaporation plants have been reutilized in pulp washing between the bleaching stages. In order to explore further their exploitation, secondary condensates were applied in bleaching, rather than after bleaching, in this thesis work. Pure water was partially substituted with four types of evaporation condensates as diluents in chlorine dioxide (D) and ozone (Z) bleaching stages. Mass and COD balance of the bleaching stages and the effects of secondary condensates on pulp quality and chemical composition were studied.

Headspace gas chromatography - mass spectrometry was applied for quantifying volatile organic compounds (VOCs) in the condensates, bleaching filtrates and the vapor phase of the bleaching reactor. Meanwhile, COD of pulp filtrates and condensates and brightness, viscosity and kappa number of the pulps were examined to study the possible impacts of the condensate use on environmental load and pulp properties.

No noticeable effect of the condensate used on pulp brightness, viscosity and kappa number in D_0 and Z stages were observed. The main VOCs in the condensates were methanol, ethanol, acetone and some sulphur components, such as dimethyl disulfide. VOCs detected in pulp filtrates were mainly methanol. Also, the condensate-free pulp filtrates contained significant amounts of methanol, thus secondary condensates are not the only source of methanol. It could also be formed through demethoxylation of lignin in pulp bleaching. Instead of the secondary condensates, the unbleached kraft pulp was the main source of sulphur in pulp bleaching. Secondary condensates and the methanol in them contributed quite little on COD of pulp filtrates. In conclusion, it seemed to be feasible to substitute fresh water with secondary condensates in pulp bleaching.

Key words: secondary condensate; chlorine dioxide; ozone; mass balance; ISO brightness; viscosity; kappa number

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Espoo, May, 2017.

Yang Wang

ABBREVIATIONS

SC	Secondary Condensate
GC-MS	Gas Chromatography - Mass Spectrometry
D_0	Chlorine Dioxide Bleaching
UV-Raman	Ultraviolet Raman Spectroscopy
DMDS	Dimethyl Disulfide
DMS	Dimethyl Sulfide
MCM	Medium Consistency Mixer
PI Diagram	Piping and Instrumentation Diagram
IS	International Standard
HexA	Hexenuronic Acid
TCF	Total Chlorine Free
ECF	Elementary Chlorine Free
O	Oxygen Delignification
Z	Ozone Bleaching
TIC	Total Ion Chromatography
SIC	Selected Ion Chromatography

CONTENTS

1. INTRODUCTION

In traditional pulp mills, the usage of fresh water is high. Amount of water consumed in kraft pulp bleaching in late 1900s was about 18-20m^3/ADt (Pekkanen, 1996a). The recycle and reuse of effluents are necessary, and they are demanded for economic and ecological aspects.

In earlier studies, basic composition of secondary condensates was explored as well as reuse of the secondary condensates. The feasibility of using condensates from evaporators in bleaching stages were proved by several previous works. In Pekkanen and Kiiskilä's study, condensates could be used in recausticizing plant and for brown stock washing stages, which have already been applied in bleaching industry. (M. Pekkanen & E. Kiiskilä, 1996) Condensates used as brown stock washing water substitute clean hot water (Pekkanen, 1996a). Pekkanen & Kisskilä's work showed that there are no detrimental effects on pulp properties and Niemelä et al. proved that there was no unpleasant odour transferred into pulp (Niemelä, 2000, Pekkanen, 1996a). Moreover, the study of using secondary condensate as a process water in D_0 (chlorine dioxide bleaching) bleaching stage has been reported by Sankari et al. (Sankari, 2004). The effects of different components of secondary condensates on ClO_2 bleached pulp properties was explored in detail in the mentioned study. Conclusion of the work was that the use of secondary condensates is an option for process water use in D_0 bleaching stage.

The main target of this work was to determine the material balance for the main components of secondary condensates when these are applied as diluents in pulp bleaching. Industrial secondary condensate samples from different effects of black liquor evaporation were used in the study. Main components of the secondary condensates were traced over chlorine dioxide and ozone bleaching stages separately. Additionally, the pulp properties, including viscosity, brightness and kappa number, were measured to see the effects of the use of the secondary condensates on properties of the bleached pulps. To approximate the environmental load of replacing fresh water by secondary condensates, COD_{Cr} (chemical oxygen demand) of the secondary condensate samples and the bleaching filtrates were determined.

2. LITERATURE REVIEW

2.1 Secondary Condensates from Black Liquor Evaporation

Secondary condensate is the condensate of secondary vapor from a process stream (Sebbas, 1987). Kraft secondary condensates are produced through condensation of vapors from the digester or multiple effect black liquor evaporation plant (Blackwell, 1979). The utilization of secondary condensates as process water has been studied in order to close the water cycle in pulp mills and reduce their emissions. In the past years, secondary condensates have been used for brown stock washing or for washing pulp prior to its bleaching. The possibility of using condensates in pulp bleaching to replace fresh water has been carried out (Pekkanen, 1996b).

2.1.1 Chemical Composition of Secondary Condensates

Condensates from black liquor evaporation typically contain alcohols (e.g. methanol), acids (e.g. formic acid, acetic acid), ketones (e.g. acetone), terpenes (e.g. α-pinene, β-pinene), sulphur-bearing compounds (e.g. dimethyl sulfide and dimethyl disulfide) (Blackwell, 1979). Volatile compounds evaporated from black liquor along with water account for a large percentage of the organic material in the condensates (Blackwell, 1979). Sulphur bearing compounds, which are the main source of odor in black liquor, can be mostly removed by stripping and condensation. Blackwell et al. (1979) reported that H_2S, dimethyl sulfide (DMS), dimethyl disulfide (DMDS), terpenes, etc. are the main volatile components of black liquor.

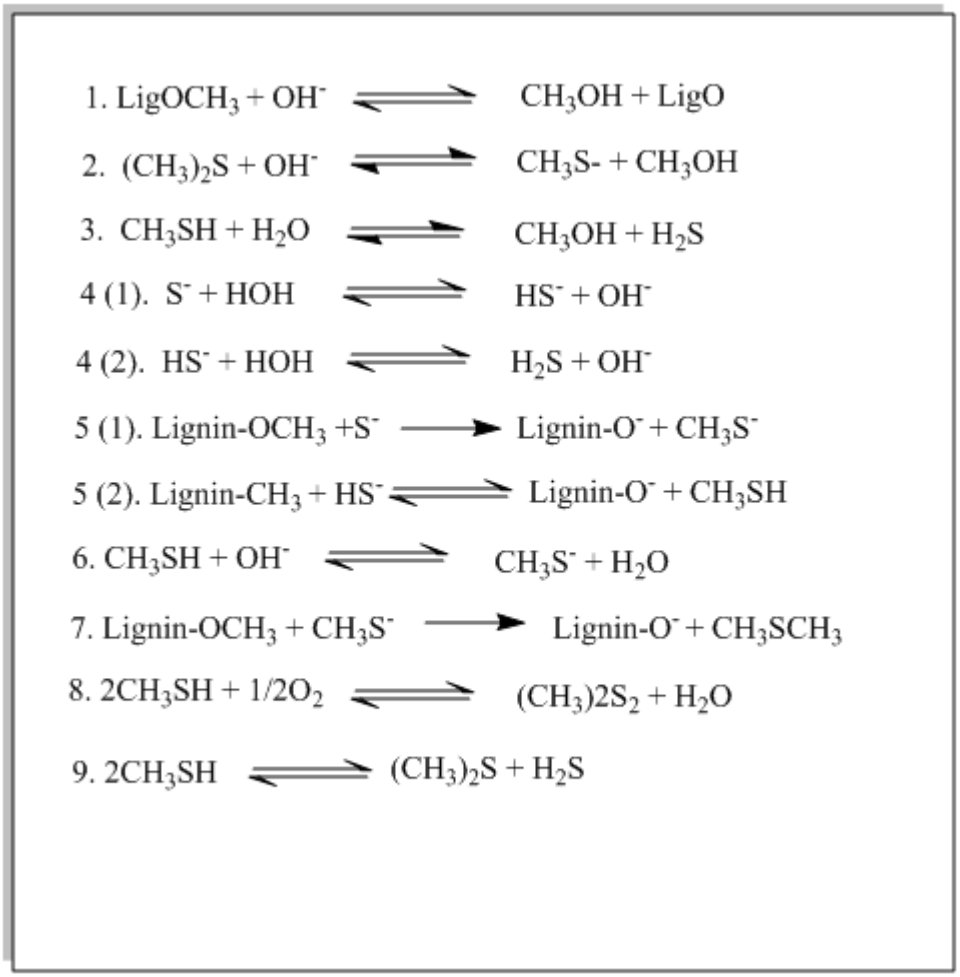
2.1.2 Component Resources

The volatiles, like alcohols, terpetenes, and sulphur compounds, exist in wood initially or they are formed through various reactions during kraft pulping. Methanol is formed due to the alkaline cleavage of 4-O-methylglucuronic acid residues in hemicellulose (Blackwell, 1979). Several investigations indicated that the alcohol content in the condensate streams in hardwood pulping process was higher than in softwood pulping process (Blosser, 1978). For instance, when a mixture of 80 % alder and 20 % Douglas fir was used as the raw material, the methanol content was 5.3 pounds per ton in the multiple-effect evaporator condensate. Pulping of 100 % Douglas fir yielded 3.6 pounds methanol per ton of the corresponding condensate (Blosser, 1978). The methanol formation in hardwood pulping was indeed higher than in softwood pulping (Wilson, 1972). Besides, methanol can theoretically be formed from lignin either directly or through dimethyl sulfide or methyl mercaptan (Reactions 1-3). However, the probability of Reactions 1 and 2 are is quite small (McKean, 1965); and the occurrence of Reaction 3 has not been verified yet (Hynninen, 1971).

The origin of ethanol can be aerobic fermentation inside round wood (Blackwell, 1979). Ethanol was traced in logs one or two weeks after the trees were felled (Wilson, 1972). Depending on the storage of the wood raw material, the concentration of ethanol may vary depending on its volatilization losses (Blackwell, 1979).

The sulfur-bearing compounds of black liquor originate from Na_2S used as the cooking chemical. These compounds are formed by Reactions 4-8 (Blackwell, 1979). Some other sulfur-bearing compounds can also be formed but their share is negligible (Blackwell, 1979).

Reaction 9 is a secondary reaction which explains that hydrogen sulfide and DMDS can also be generated from methyl mercaptan (Hynninen, 1971). Methyl mercaptan and its derivatives are formed through demethylation of lignin methoxyl groups (Wilson, 1971).



The terpenes are initially present in the wood raw material although some of them are products of the naturally occurring terpenes (Wilson, 1971). The concentration of terpenes in the condensates varies depending on the wood species in the raw material (Drew, 1966, Hurtfiord, 1967). Typically, α-pinene is the main species present in condensates. However, some other terpenes, e.g. β-pinene and α-terpineol, may also exist in the condensates in relatively high concentrations (Blackwell, 1979).

2.1.3 Evaporator

In present pulping mills, mostly multiple-effect evaporators are used. Figure 1 illustrates the operation of a conventional 7-effect evaporating plant, which produces four different secondary condensate streams. In this case, effect one consists of three bodies. Between effect one and effect two, there is a stripping column. The secondary steam from the preceding effect evaporator is used for stripping. The position of stripping column depends on its pressure need (Honkanen, 1998). In this study, secondary condensate 1 sample (SC1) was taken from effects 2-4. Secondary condensate 2 sample (SC2) was taken from effect 5. Secondary condensate 3 sample (SC3) was collected from effects 6 and 7 and the surface condenser,

and secondary condensate 4 (SC4) was collected from effect 1. Among these four secondary condensate samples, SC1 was the cleanest one, while SC4 was the dirtiest of the condensates.

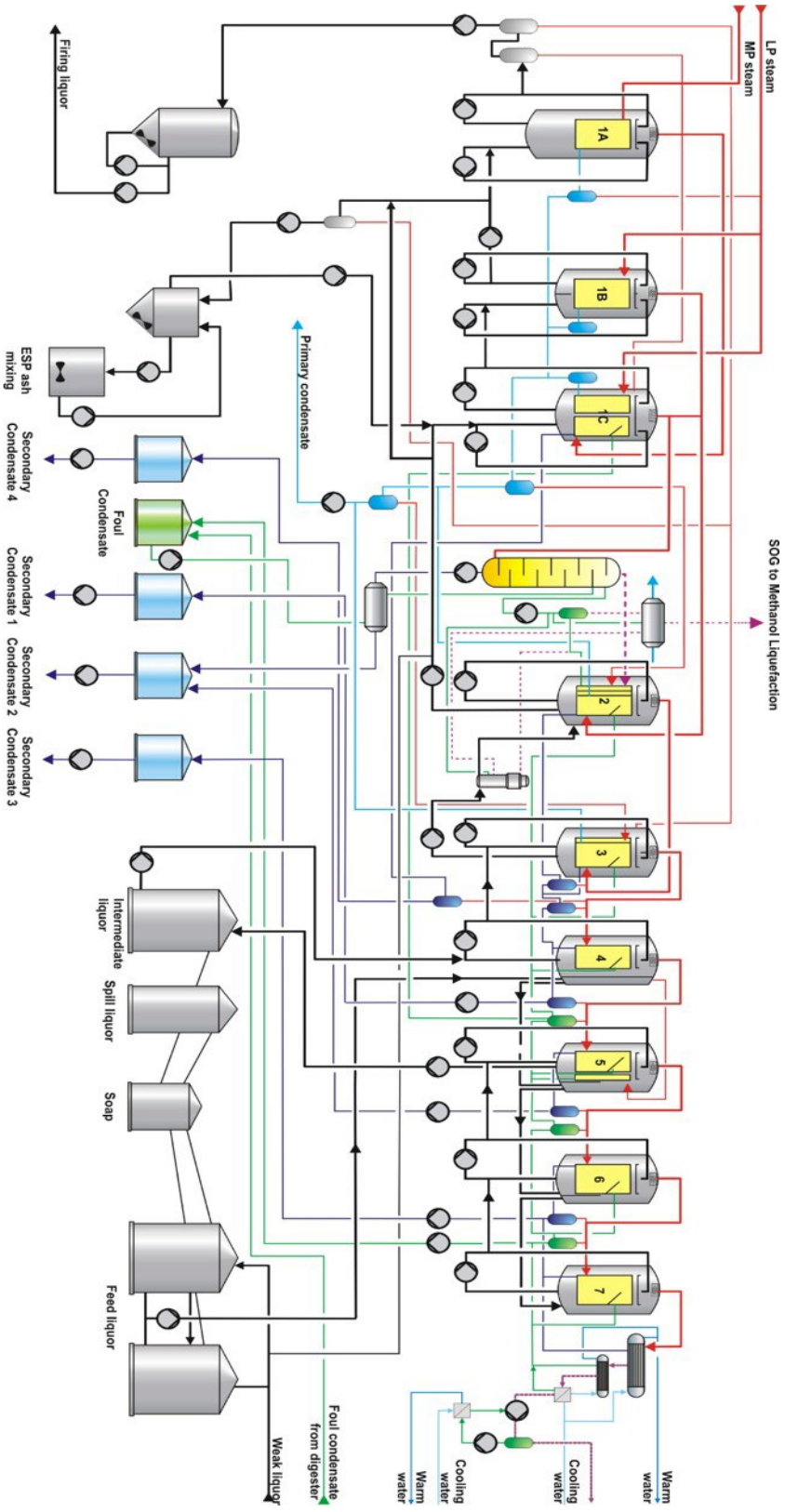


Figure 1. Flowsheet of a conventional 7-effect black liquor evaporator.

2.1.4 Environmental load of secondary condensates

The environmental impact of pulp mill effluents is monitored by their COD (chemical oxygen demand) and BOD (biological oxygen demand) levels. Recently, the standard of acceptable COD emissions has become stricter. Therefore, the control of emissions and reuse of various process streams is considerably more critical. Besides, the toxicity of some of the compounds present in the condensates forms another criterion for the environmental control. For instance, hydrogen sulfide can be toxic to fish at 1 ppm concentration (Haydu, 1952) and methyl mercaptan shows toxicity to fish at 0.5 ppm concentration (Cole, 1935, Haydu, 1952). The sulfur compounds can cause unpleasant odor during the processing or in the end products, and toxicity even at a very low concentration (Mattsson, 2009).

2.1.5 Previous studies of condensates on different bleaching stages

There were some studies on utilization of condensates, including secondary and foul condensates, in different bleaching stages, many years ago. Those studies mostly focused on use of the condensates in pulp washing and their effects on the pulp properties and the odor problem. In Niemelä et al.'s (2000) study, condensate impurities were analyzed by capillary gas chromatography – mass spectrometry (GC/MS) and typical pulp properties were measured after utilizing the condensates in late washing stages (Niemelä, 2000). Results showed no obvious effect on pulp properties when only secondary condensates were applied. On the contrary, negative effects on pulp properties were detected, if mixtures of foul and secondary condensates were applied. Pekkanen and Kiiskilä made a similar conclusion on the possibility of applying the condensates in washing after the bleaching stages (Pekkanen, 1996b).

Sankari et al. studied the possible use of secondary condensates as a process water in D_0 bleaching stage (Sankari, 2004). They identified no major deterioration in the typical pulp properties (kappa number, viscosity, brightness) by the secondary condensates. In fact, the bleaching result was related with the additional COD load value. Consequently, the more COD load was added, the worse the bleaching result was, especially expressed in kappa number and viscosity (Sankari, 2004). However, alcohol, acetone, formic acid and acetic acid had almost no negative impact on the pulp properties. The most harmful impurities in secondary condensate were the sulphur-based components (Sankari, 2004).

2.2 D_0 and O_3 Bleaching

This section displays the concept of bleaching, its development and parameters that affect the bleaching efficiency. Besides, details of D_0 and Z (O_3) bleaching stages are illustrated as well.

2.2.1 Brief introduction of bleaching

Bleaching is a procedure, which can improve the brightness of pulp after the pulping process through the action of chemical agents. Brightness is an optical property which shows the reflectance of visible light from pulp fibers or paper sheets (Reeve, 1996c). The brightness of paper is one of its most important properties that affects the printability of paper. Besides, bleaching also can purify pulp fibers and broaden their application range (Reeve, 1996c).

Objectives of bleaching must be archived without decreasing the final fiber strength, which is the reason why the bleaching method, operation conditions, and process control are so important (Reeve, 1996c).

Before the 18th century, people bleached paper in natural condition with the assistance of sunlight (Shan, 2008). Chlorine gas and its ability for bleaching was discovered by Scheele in 1774 in Sweden (Reeve, 1996c). Since then many bleaching methods and chemicals were used, e.g. Cl_2, $Ca(OCl)_2$. and some organic chlorine compounds, etc. However, chlorine was not finally the best option since it generates harmful organochlorines, such as dioxins, which are toxic and pollute the environment. The dioxins are very stable compounds that accumulate in the living organisms harming them. Thus, ECF (elementary chlorine free) and TCF (total chlorine free) bleaching sequences are used nowadays in combination with other processes, e.g. oxygen delignification. Besides chlorine dioxide, hydrogen peroxide and ozone are the most popular, efficient and environmentally friendly bleaching chemicals.

Water plays important roles in pulp bleaching. To distribute bleaching chemicals evenly in pulp suspensions, water is needed to adjust the consistency of the pulp suspension and dissolve the bleaching chemicals (Reeve, 1996c).

2.2.2 Chlorine dioxide bleaching

Chlorine dioxide is an unstable and explosive gas that can be stored few days in maximum, at a low temperature, before using in bleaching. The common methods to get chlorine dioxide base either on chlorate ion (ClO_3^-) reduction or chlorite ion (ClO_2^-) oxidation (Reeve, 1996a).

$$ClO_3^- + 2\,H^+ + e^- \longrightarrow ClO_2 + H_2O$$
$$ClO_2^- \longrightarrow ClO_2 + e^-$$

As a bleaching agent, ClO_2 has high selectivity towards lignin. When added into hot pulp suspension, it will easily vaporize. To avoid that, the ClO_2 bleaching towers are designed to keep the chlorine dioxide in solution by a significant hydrostatic pressure at the chemical addition point (Reeve, 1996a).

Most of the bleaching chemicals react with the pulp through oxidation reactions (Sixta, 2006). Chlorine dioxide oxidizes and dissolves lignin thus enhancing the brightness of pulp. The reactivity of chlorine oxide with phenolic lignin is higher than with non-phenolic lignin. During the bleaching process, chlorine oxide is reduced step by step with several intermediate products produced before the chloride ion is finally formed (Reeve, 1996a). The parallel formation of chlorate ion (ClO_3^-) as another stable product decreases the bleaching efficiency. Hypochlorous acid (HOCl), formed *in situ*, leads to the formation of chlorinated organic compounds, a kind of absorbable organic halogens in solution (AOX) or organically bound halogens in the pulp (OX) (Reeve, 1996b). In addition to removing lignin, chlorine dioxide may react with chromophoric structures in lignin, thus bleaching it (Reeve, 1996a). Figure 2 illustrates the reactions of chlorine dioxide in delignification and bleaching processes (Reeve, 1996a).

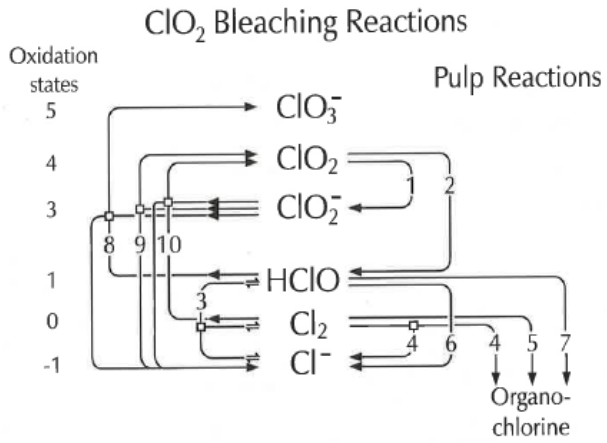


Figure 2. Reactions of chlorine dioxide with pulp in the process of bleaching (Reeve, 1996b)

2.2.2.1 Effects of pH on ClO_2 bleaching

pH and temperature affect the bleaching efficiency and the end product properties. pH is a critical parameter on almost every bleaching stage.

In chlorine dioxide bleaching, the bleaching result can be monitored through kappa number. The *in situ* formed chlorite ion does not react further to form active bleaching chemicals (HOCl or ClO_2) if the final pH is higher than 4. Therefore, a too high pH level may lower the bleaching efficiency through a partial loss of the bleaching potential. Many authors have proved that pH is a sensitive factor for chlorine dioxide bleaching, when the end pH value varies in the range of 2-4 (Reeve, 1996b). The delignification efficiency of chlorine dioxide is highest and the chemical losses lowest at end pH < 4 (Reeve, 1996b). The bleaching pH can be set as 3.5-4 if the highest brightness is needed, and at this pH value, the loss of effective chlorine is in minimum as shown in Figure 3 (Shan, 2008).

2.2.2.2 Effect of time on ClO_2 bleaching

The consumption of the active bleaching chemical and the brightness development are enhanced while the retention time increases (Reeve, 1996a). Traditionally, an industrially designed CEDED bleaching sequence had three hours retention time. In an upflow - downflow bleaching tower, the retention time in upflow side was 30 minutes and pulp remained in the downflow side for 2.5 hours to reach ideal brightness and bleaching efficiency (Reeve, 1996a). Increased production capacities and many other factors have later changed the design of the bleaching towers and their retention times.

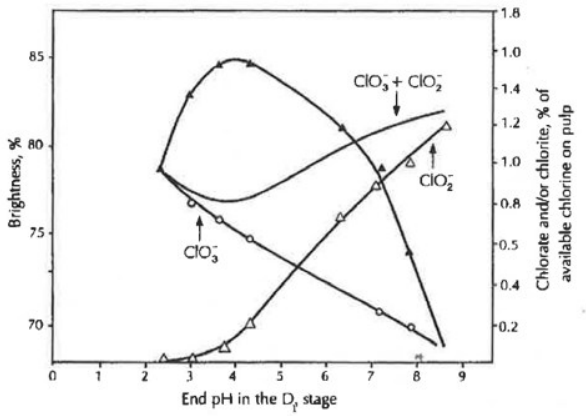


Figure 3. The impact of end pH in D_1 stage on brightness development and chlorite and chlorate formation (Rapson, 1979)

2.2.2.3 Effect of temperature on ClO_2 bleaching

Typical temperature of chlorine dioxide bleaching stage is around 70 ºC. Increasing the reaction temperature leads to higher brightness and lower residual chemical content at a given chlorine dioxide dosage (Reeve, 1996a).

The higher temperature limit of chlorine dioxide bleaching usually depends on the practical feed steam temperature (Reeve, 1996a). Besides, temperature can be affected by the addition of chlorine dioxide. When 5 ºC chemical is added into 70 ºC pulp at certain consistency, temperature will drop accordingly (Reeve, 1996a)

2.2.3 Ozone bleaching

Comparing with chlorine-based bleaching agents, ozone has higher oxidation power and its capacity of increasing brightness is better. Besides, effluents of ozone bleaching contain no or little organochlorines and the chloride-free waters are easier to cycle (Sixta, 2006). These advantages increase the attractiveness of ozone as a bleaching agent. However, ozone has also drawbacks in comparison with chlorine dioxide. Ozone decomposes easily and it must be produced on mill site by passing oxygen gas through electrical discharge. Recent technology makes the ozone production easier with high power efficiency and therefore ozone is becoming a more and more competitive bleaching chemical nowadays.

2.2.3.1 Ozone production

Figure 4 illustrates the principal of ozone bleaching from the generation of ozone to its destruction. The production system of ozone depends on the ozonation consistency, the oxygen source, the temperature of cooling water, etc. (Sixta, 2006). Typically, ozone is produced by silent electrical discharge from an oxygen-containing gas in an ozone generator. Ozone is preferably from pure oxygen gas since it can lead to high ozone concentration with little side products (Sixta, 2006).

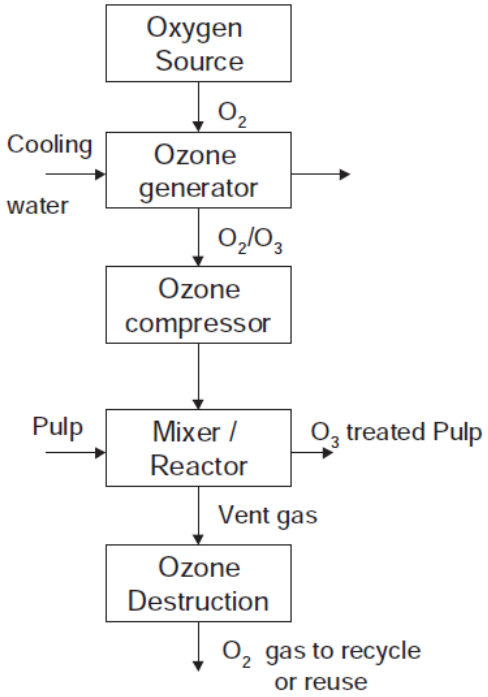


Figure 4. Ozone system in pulp bleaching (Owen, 1996)

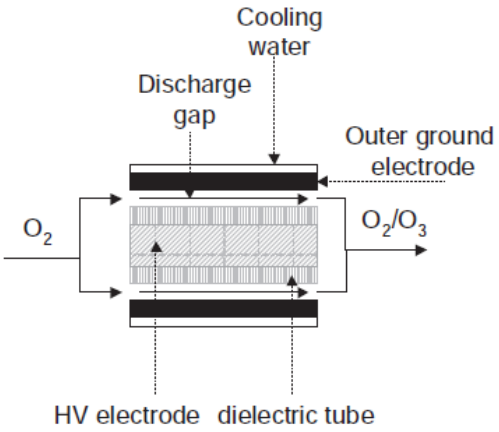


Figure 5. Ozone production process from oxygen (Sixta, 2006)

Figure 5 illustrates an ozone production system schematically. Oxygen gas flows through the discharge gap between the outer ground electrode(s) and the inner high voltage (HV) electrode coated with a dielectric material. The electron discharge decomposes oxygen gas to oxygen radicals, which then combine with oxygen molecules to form ozone. The ozone generator design, the cooling system, the voltage and frequency of the applied alternating current, and the dielectric material are critical for the performance of the system.

2.2.3.2 Effect of pH on O_3 bleaching

Similar to chlorine dioxide bleaching, several factors affect the efficiency of ozone bleaching. These most important factors relevant for the bleaching results include pH, temperature, ozone dosage, pulp consistency and COD carry over (Sixta, 2006). It is generally agreed that pH < 3 is optimal for ozone bleaching performance (Rutkowski, 1984). It has been proved that ozone bleaching efficiency is 6 times higher at pH 2.5 than at pH 10 (Roncero, 2003). Thus, pH 2-3 range is generally applied for industrial ozone bleaching. To reach this low pH, pulp suspension needs to be acidified by sulfuric acid prior to the bleaching (Sixta, 2006). Lindholm proved that keeping pH around 3 enhanced lignin removal efficiency without any negative effect on pulp viscosity (Lindholm, 1987). Besides, ozone is more stable at the lower pH range. According to Pan et al. only 5% of ozone self-decomposed in 10 min at pH 3 in comparison with 33% decomposition at pH 7 (Pan, 1984).

2.2.3.3 Effect of temperature on O_3 bleaching

The temperature range applied in industrial ozone bleaching is 40-55℃ (Sixta, 2006). High temperatures impair ozone bleaching capacity through more pronounced decomposition of ozone (Sixta, 2006). Many studies have concluded that higher temperature could affect negatively the selectivity and efficiency of delignification by ozone (Sixta, 2006). Chandra found that the best ozone delignification performance was achieved at 23℃ (Sixta, 2006), similar to the observations by Soteland (Soteland, 1984) and Liebergott et al. (Liebergott, 1992). Allision R.W. reported on a slightly reduced delignification of radiata pine kraft pulp by ozone at 80℃ (34.7% lignin removal) in comparison with delignification at 29℃ (37.1%) (Sixta, 2006). In contrast, Lindquist observed that raising temperature from 30℃ to 80℃ had no effect on the selectivity of ozone bleaching stage (Lindqvist, 1982, Lindqvist, 1984).

Figure 6 presents the effects of temperature in ozone stage, in which the reduction of viscosity was constantly enhanced with increasing temperature and delignification was retarded when temperature was raised above 55℃. As conclusion, the delignification efficiency at high temperature, e.g. above 55℃, is decreased and the possible reason could the more pronounced ozone decomposition at the high temperature (Sixta, 2006).

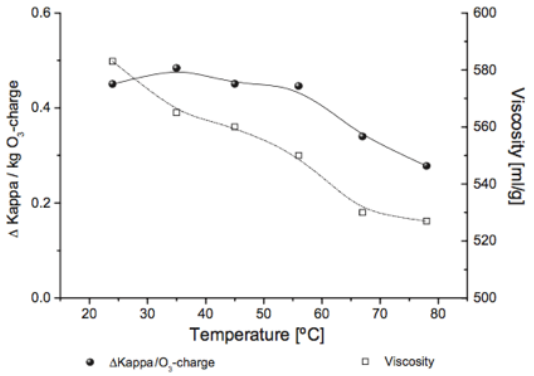


Figure 6. Effect of temperature on delignification efficiency (△kappa/O_3 charge) and viscosity (Sixta, 2006).

Pulp: E/O-pretreated beech dissolving pulp with acid sulfite treatment, kappa number 1.9, viscosity 627 ml/g; medium consistency (10 %) ozone bleaching, pH 2.5, 10s mixing time;
Ozone charge: 2.2 – 2.3 kg/odt, carry over: 5 kg COD/odt (Sixta., 1995)

2.2.3.4 Pulp Consistency on O_3 bleaching

The industrial medium consistency (ca. 10 %) ozone bleaching technology was established in 1992 (Sixta, 2006) and it is nowadays generally applied in the pulp industry (Dillner, 1992, Sixta, 1994). Although some mills apply the high consistency (around 35%) ozone bleaching technology around the world, bleaching at medium consistency is still the dominate technology (Table 1). Figure 7 presents the process flowsheet for medium consistency bleaching. In principle, H_2SO_4 is mostly used for pH adjustment and mixed with pulp from previous stage (Vuorinen, 2007). O_3 is dosed into the acidified pulp with a high-shear mixer. After a short delay in the ozonation reactor the bleaching reactions are completed and the residual can be removed before washing the pulp for the next stage (Sixta, 2006).

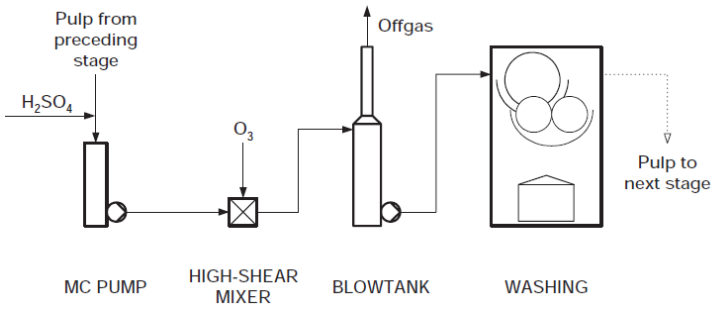


Figure 7. Process flowsheet of a typical medium consistency ozone bleaching stage (Sixta, 2006)

Table 1. Ozone bleaching installations in the year 2004 (Sixta, Suess et al. 2006)

Mill	Location		Bleaching sequence	Z-Stage consistency	Process supplier	Ozone generator manufacturer	Pulp process, Pulp grades	Ozone charge [kg t^{-1}]	Pulp capacity [adt · 10^{-3} a^{-1}]
Lenzing AG	Lenzing	Austria	(EOP)ZP	MC	Kvaerner	WS-OT	HW-Sulfite, DP	2	230
Lenzing AG	Lenzing	Austria	(EOP)ZP	MC	Kvaerner	WS-OT	HW-Sulfite, DP		
Union Camp	Franklin, VA	USA	OZ(EO)D(EP)D	HC	Sunds	Ozonia	SW-Kraft, P		300
Södra Cell	Monsteras	Sweden	OQ(OP)(ZQ)(PO)	MC	Kvaerner	Trailigaz	SW-, HW-Kraft, P	2	700
Wisaforest	Pietarsaari	Finland	O(ZD)(EO)(ZD)(EP)D	MC	Ahlström	Trailigaz	SW-, HW-Kraft, P	2	630
M-real Husum	Husum	Sweden	OQPZD	MC	Ahlström	Ozonia	HW-Kraft, P		690
Metsä-Botania	Kaskinen	Finland	OQZQ(EOP)ZP, OD(EOP)ZP	MC	Ahlström	Ozonia	SW-, HW-Kraft, P		425
Peterson Seffle	Säffle	Sweden	ZEP	MC	Kvaerner	WS-OT	SW-Sulfite, P	6	50
Bahiapulp	Camacari	Brazil	(OO)AZP	MC	Kvaerner	WS-OT	HW-PHK, DP	4	120
SCA Östrand	Timra	Sweden	OOQ(OP)A(ZQ)(PO)	HC	Sunds	Ozonia	SW-Kraft, P		400
Sappi	Ngodwana	South Africa	OA(ZD)(EO)D	HC	Andritz, Sunds	Ozonia	SW-, HW-Kraft, P		240
Ponderosa Fibers	Memphis, TN	USA	ZPZP	MC	Ahlström	Ozonia	Recycled Fibers		60
Metsä-Rauma	Rauma	Finland	OO(ZQ)(PO)(ZQ)(PO/PO)	MC	Ahlström	WS-OT	SW-Kraft, P		550
Stora Enso North America	Wisconsin Rapids	USA	OAZ(EO)DD	HC	Sunds	Ozonia	HW-Kraft, P		240
Votorantim	Luiz Antonio	Brazil	OO(ZD)(EOP)D	MC	Kvaerner	Ozonia	HW-Kraft, P	4	350
Votorantim	Jacarei	Brazil	OQ(OP)(ZE)D	MC	Kvaerner	Ozonia	HW-Kraft, P	4–5	280
Klabin	Monte Alegre	Brazil	OQ(OP)(ZQ)(PO)	MC	Kvaerner	WS-OT	SW-, HW-Kraft, P	4	140
Matussiere (Research)		France		HC		OZONIA	recycled		
Domtar	Espanola	Canada	OA(ZD)E(Dn)D	MC	Ahlström		HW-Kraft, P	3–6	370
ZPR Rosenthal	Blankenstein	Germany	(OO)Q(OP)(DQ)Z(PO)P	HC	Sunds	WS-OT	SW-Kraft, P		280
Burgo Ardennnes	Virton	Belgium	(OO)D(Z(EO))(DD)	HC	Sunds	Ozonia	HW-Kraft, P		400
Nippon Paper	Yufutsu	Japan	O(ZD)(EOP)D	MC	Andritz	Ozonia	HW-Kraft, P		175
Nippon Paper	Yatsushiro	Japan	O(ZD)(EOP)D	MC	Andritz	Wedeco	HW-Kraft, P		210
Oji Paper	Nichinan	Japan	OaZEPD	HC	Metso	Ozonia	HW-Kraft, P		262
Votorantim	Jacarei	Brazil	OA(ZE)DP	HC	Metso	Wedeco	HW-Kraft, P		735
Glatfelter	Spring Grove	USA	O(ZD)(EOP)D	LC	Andritz	Wedeco	HW-Kraft, P		223
Neusiedler SCP	Ruzomberok	Slovakia	OO[A](ZEOP)(D_nD)	HC	Metso	Wedeco	SW-, HW-Kraft, P	3–4	370
Total	Total								8430

HW = hardwood, SW = softwood; MC = medium-consistency,
HC = high-consistency.
DP = dissolving pulp.
P = paper pulp

2.3 Analysis of Secondary Condensate Effects in Bleaching

This section explains how the effect of condensates can be analyzed through head space gas chromatography - mass spectrometry (GC-MS) and chemical oxygen demand (COD) measurement.

2.3.1. GC-MS Technique

Headspace GC-MS is a widely employed technique to determine various volatile organic compounds, such as pesticides, halogenated compounds, etc. (Santos, 2002, Santos, 2003). It is a sensitive technique and can be automated (Swartz, 1998, Luis, 2013). In GC, chemical compounds in a sample are separated from each other based on their volatility and retention on the stationary phase of a long capillary column. The volatility range of compounds to be separated is controlled by the column oven temperature program. The lower boiling point compounds are eluted faster they appear in the chromatogram earlier than the higher boiling point compounds.

In GC-MS, the flow from the GC column is led directly to the ionization chamber of MS. An electron beam is usually applied for the ionization of the sample molecules after which the ions are separated based on their mass-to-charge ratio (m/z). Besides their molecular ions, the sample molecules can form specific fragments that can be utilized in identification of the molecular structure. Figure 8 illustrates how MS works in principle. As a sampling technique, headspace injection can be used for measuring thermodynamic vapor-liquid phase equilibria (VLE), and determining volatile compounds in liquid samples (Luis, 2013). By heating samples firstly at specific temperature to VLE in a vial (Figure 9), VOCs are sampled automatically to GC (Luis, 2013).

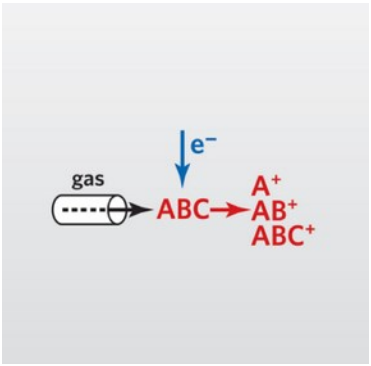


Figure 8 . Working principle of mass spectrometry. (EAG, 2016)

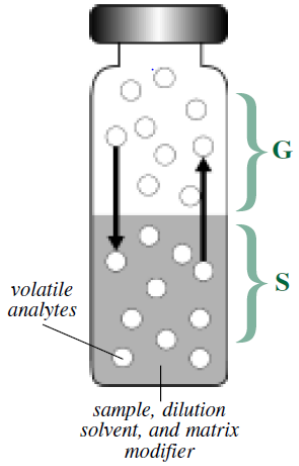


Figure 9. Illustration of the headspace vial (RESTEK, 2016)

The carrier gas carries samples through a coiled column, in which the sample molecules are separated from each other (Figure 10). Selection of the column is the most critical factor for the separation that depends mainly on the dimension of the column and polarity of the stationary phase (States, 2016).

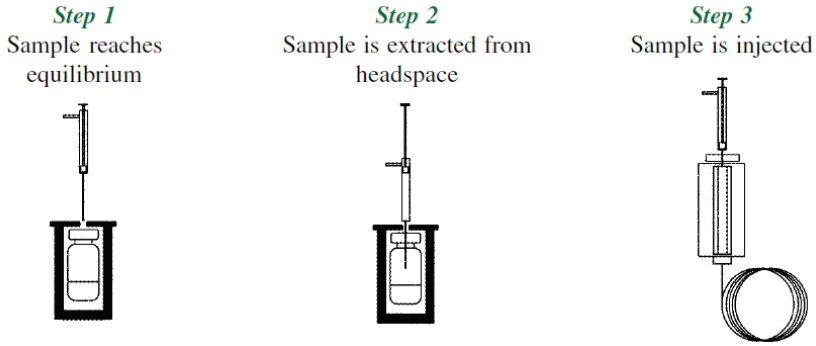


Figure 10. Gas syringe system and sampling process (RESTEK, 2016)

Almost every chemical compound has its unique mass spectrum. Based on the spectra given by MS, the unknown components can be identified and quantified through their gas chromatogram peaks.

2.3.2. Chemical Oxygen Demand

Pulp mills use COD nowadays as a washing loss parameter in their fiber lines and to monitor the performance of their biological water treatment plants. COD measures the maximum potential environmental load by the organic substances in the effluent, since the organic compounds could be ultimately oxidized into CO_2 and water. Thus the measurement of COD is applied for measuring effluent organic content (Sawyer, 2003). In COD measurement, the oxidation of organic compounds into water and carbon dioxide may differ from the biological assimilability of substances, e.g. lignin and glucose are both fully oxidized in the COD test (Sawyer, 2003). COD value is higher than biological oxygen demand (BOD) value if biologically resistant organic substrates exist in the sample (Sawyer, 2003).

Various oxidation agents have been historically used for COD measurement. Potassium permanganate has been used as oxidation agents for a long time and it has been proved that there was large variation in the oxygen consumption depending on the type of compounds, and the oxidation degree was varied with the reagents applied (Sawyer, 2003). Besides potassium permanganate, ceric sulfate, potassium iodate and potassium dichromate have been studied as oxidation agents (Sawyer, 2003). Dichromate has been proved to be the most suitable one, since it can completely oxidize large number of organic compounds into CO_2 and water (Sawyer, 2003).

2.4. Summary of Literature Review

The literature review provides background information on black liquor evaporation condensates and their internal uses, bleaching methods, and analytical methods that are relevant for the research topic. In conclusion, the use of secondary condensates in late washing stages of pulp bleaching line was proved feasible (Pekkanen, 1996b, Niemelä, 2000). Meanwhile, no noticeable drawbacks were observed in using secondary condensates in D_0 bleaching stage (Sankari, 2004). However, very little or no information is available on the effect of secondary condensates on the mass balances over the bleaching stages where they have been applied. Previous studies have applied GC-MS as the main analytical technique for identifying and quantifying the chemical components of the condensates.

3. MATERIALS AND METHODS

This chapter describes materials and methods that were used for the experiments. The source and details of the materials are talked, and also the operation conditions and parameters of each experiment in this thesis work.

3.1. Materials

3.1.1. Secondary condensates

Four secondary condensate samples were obtained from industry (Figure 11). They were collected from different effects of a single evaporation plant, the flow sheet of which is presented in 2.1.3. SC1 was from Effects 2-4; SC2 was from Effect 5; surface condensate SC3 was from Effects 6 and 7; whilst SC4 was from Effect 1. All the condensates were stored in a fridge at 5 ºC in glass bottles that were tightly closed to protect VOCs from escaping.

Figure 11. Four secondary condensates obtained from industry in transparent bottles. (From left to right: SC1 to SC4)

3.1.2. Pulp for bleaching

Unscreened oxygen delignified birch kraft pulp was obtained from industry (Figure 12). Some larger particles present in the pulp were picked out by hand. The pulp was stored in the fridge at 5 ºC. The chemical and optical properties of the pulp are presented in Table 2.

Table 2. Unbleached birch kraft pulp properties

Kappa Number	Viscosity / mg/l	ISO Brightness / %
15	1167	42.3

Figure 12. Birch kraft pulp for ozone and D_0 stage bleaching collected from industry

3.1.3. Bleaching filtrates

Bleaching filtrates were collected from laboratory bleaching trials for further COD and GC-MS analyses (Figure 13). There were 10 pulp filtrates in total, five filtrates from D_0 bleaching and five filtrates from ozone bleaching. One of the five bleaching trials in each case was performed without a secondary condensate addition and the rest four with additions of SC1, SC2, SC3 and SC4.

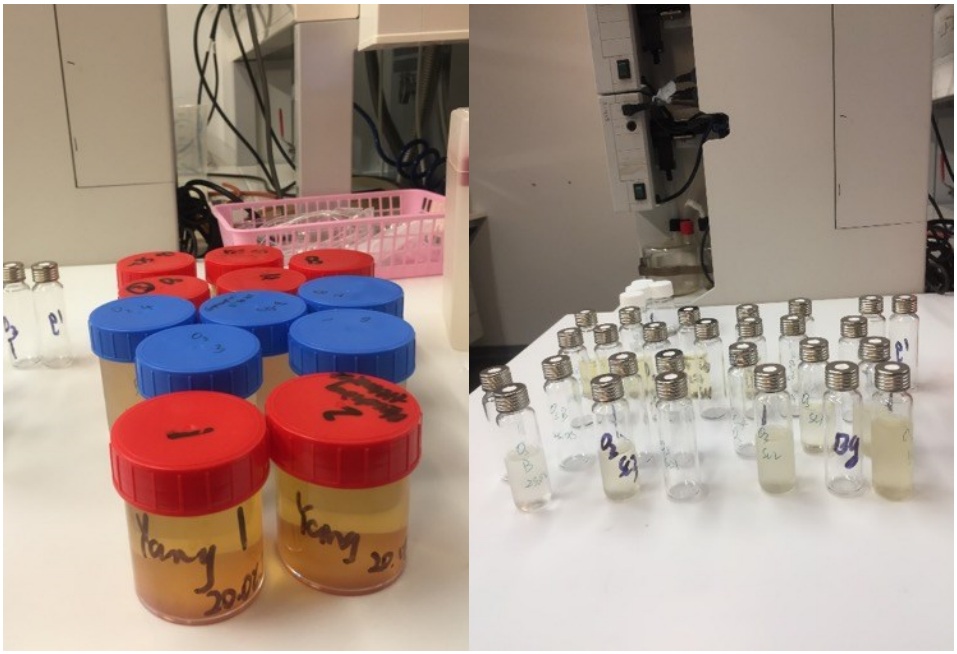


Figure 13. Pulp filtrates and vapor phase samples after bleaching

3.1.4. Vapor phase samples after bleaching

Vapor phase samples (Figure 13) were collected after each bleaching trial in medium consistency mixer (MCM) reactor (Figure 16). During the sampling, the MCM reactor was kept closed while the vapor was collected by opening the top valve, which was connected with a transparent sampling tube. The vapor was collected from the sampling tube with a syringe the content of which was then transferred into a headspace vial for GC-MS (Figure 14). The dead volume of the sampling line was taken into account by discarding the initial flow through the line.

Figure 14.Vapor phase sample collection system

3.2. Materials Preparation

3.2.1. Intermediate Reference Solutions for GC-MS Analysis

To test the GC-MS analysis for the relevant volatiles (Table 3), solutions of acetone, ethanol, methanol, methyl mercaptan, dimethyl sulfide, dimethyl disulfide and dibromomethane (internal standard) were prepared in different ratios.

Table 3. Characteristics of compounds reported to be present in secondary condensates (Design Institute for Physical Properties, 2005; 2008; 2009; 2010; 2011; 2012; 2015; 2016)

	Boiling Temperature / ℃	Structural formula	Solubility
Methanol	64.7	CH_3OH	water
Ethanol	78.29	CH_3CH_2OH	water
MM	5.956	CH_3SH	ethanol
DMDS	109.75	CH_3SSCH_3	ethanol
DMS	37.33	$(CH_3)_2S$	ethanol
Acetone	56.29	CH_3COCH_3	water

DMDS is practically insoluble in water even when first dissolved in ethanol and then mixed with water. Thus, all compounds, except DMDS, were diluted to 5000 ppm in water. This stock solution was then diluted in the range of 10-100 ppm. Internal standard (IS) was added into intermediate solution at 2 ppm concentration. An intermediate solution of DMDS with IS was prepared in ethanol instead of water.

3.2.2. Condensate and filtrate sample preparation

Condensates and filtrates samples were collected and prepared with 2 ppm IS for GC-MS.

3.3. Methods

This section illustrates all the methods applied in this thesis studies.

3.3.1. GC-MS analysis for liquid and gas samples

GC-MS was applied for analyzing the secondary condensates, pulp filtrates and vapor phase samples. The head space GC-MS system consisted of Thermo Fisher GC Trace 1300 gas chromatograph, quadrupole MS ISQ mass spectrometer and Trisplus RSH head space (HS) autosampler unit (Fig. 15). The HS sampler operation parameters were: temperature 70℃, 2 min; sample loop 5 min 60℃. The GC parameters were: carrier gas (He) 1 ml/min, column Thermo Scintific TG-200 MS with temperature 30℃ for 5min and rate 1℃/min, 35℃ for 5 min; elevation at 50℃/min, then 110℃ for 1min; split ratio 1 : 100, mass transfer line temperature 250℃; ion sorce temperature 200℃, electron impact ionization 70V, scan range 10-200 amu.

Figure 15. Thermo Trace 1300 and ISQ

3.3.2. Chlorine dioxide bleaching

Chlorine dioxide (D_0) bleaching was carried out 10% pulp consistency in a MCM reactor made of titanium (Figure 16). The maximum filling capacity of reactor was ca. 2.5 L. Table 4 displays the reaction parameters that were used to simulate industrial D_0 stage.

Figure 16. MCM reactors for chlorine dioxide (left) and ozone bleaching (right)

Table 4. D_0 bleaching parameters applied

Time / min	45
Temperature / ℃	60
End pH	3
ClO_2 dosage (as active Cl) / kg/odt	30
Pulp consistency / %	10
Condensate dosage / L*	0.6
Pulp / g (as dry)	200

*applicable when adding condensates for partially replacing fresh water

3.3.3. Ozone bleaching

Ozone bleaching was carried out at 10% consistency in a Teflon lined MCM reactor (Figure 16). The reaction parameters applied are listed in Table 5. Ozone was produced on site due to its instability. The concentration of O_3 in the gas was titrated before each bleaching trial to calculate the volume of the gas to be added. The ozone-rich gas was dosaged from the storage tank to the MCM reactor by the aid of external pressure (Figures 17 and 18). Keeping uniform dosaging between the experiments was challenging and therefore a range is reported for the ozone dosage (Table 5).

Table 5. O_3 bleaching parameters applied

Time / min	45
Temperature / ℃	60
pH	3
O_3 dosage / kg/odt	3-5
Pulp consistency / %	10
Condensate dosage / L*	0.6
Pulp / g (as dry)	200

*applicable when adding condensates for partially replacing fresh water

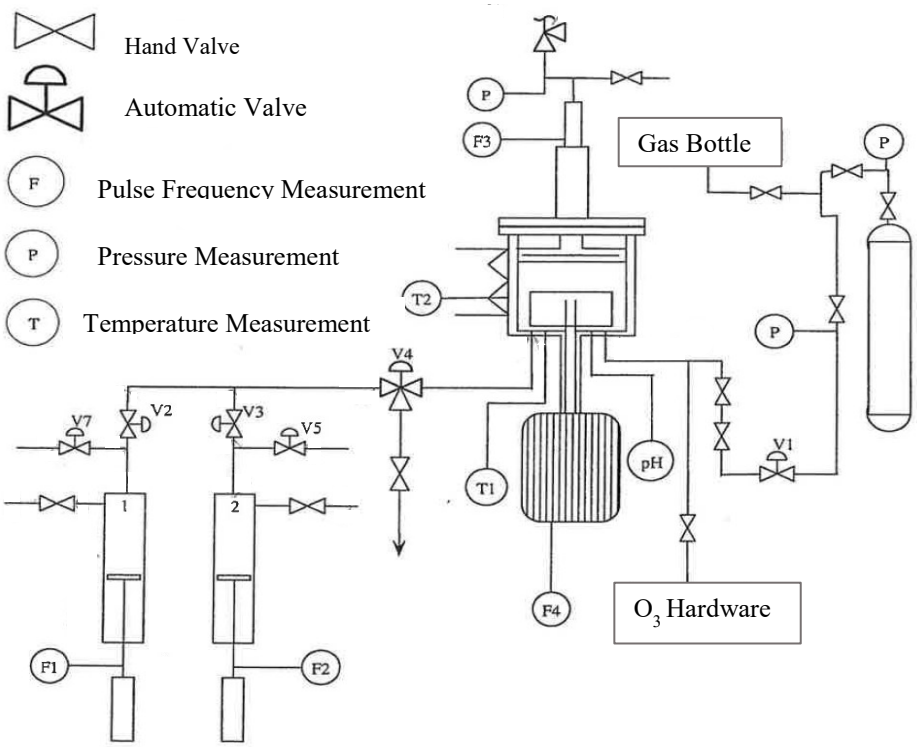


Figure 17. PI diagram of ozone MCM reactor (translation from MCM reactor instruction in Aalto University)

Figure 18. Ozone generator (left) and ozone storage tank (right)

3.3.4. Alkaline extraction

Alkaline extraction was carried out for the bleached pulps to increase the reliability of UV resonance Raman spectroscopy of the pulps. The alkaline extraction parameters applied are listed in Table 6.

Table 6. Reaction parameters of alkaline extraction

NaOH / kg/odt	10
Temperature / ℃	60
Time / min	75

3.3.5. COD

COD levels of the secondary condensates and the bleaching filtrates were measured according to standard SFS 5504. In this standard method COD should be lower than 700 mg/l, otherwise the sample should be diluted. Table 7 presents the pre-estimated COD concentrations before and after the dilutions applied.

Table 7. Dilution of condensate/filtrate samples for COD analysis

Estimated concentration before dilution mg / l	Dilution	Estimated concentration after dilution / mg/l
400	-	400
500	-	500
2000	1:4	500
4000	1:8	500

3.3.6. UV resonance Raman spectroscopy

Besides delignification, hexenuronic acid (HexA) decomposes during pulp bleaching by the action of ozone and hypochlorous acid formed *in* situ in chlorine dioxide bleaching (Vuorinen, 2007). UV Raman spectra of hardwood pulps show distinct bands for cellulose, lignin, and HexA at 1093.5, 1604.5, and 1655 cm^{-1}, respectively (Jääskeläinen, 2005). The relative band heights can be used for estimation of residual lignin and HexA contents of bleached pulps.

UV-Raman spectroscopy was performed with a Renishaw 1000 UV Raman spectrometer with Innova 90C FreD frequency-doubled argon ion laser and a Leica DMLM microscope (Afsahi, 2015). UV Raman spectra were collected at 244 nm from hand sheets of the bleached and subsequently alkali extracted pulps.

The UV Raman spectra were baseline-corrected linearly by Grams AI spectroscopy analyzing software and normalized to cellulose peak at 1094 cm^{-1} (Afsahi, 2015). The spectra were analyzed according to Jääskeläinen (Jääskeläinen, 2005).

3.3.7. Pulp properties

This section describes the methods used for characterizing the bleaching result by kappa number, viscosity and ISO brightness.

3.3.7.1. Paper sheet preparation

Paper sheets were prepared according to TAPPI standard T205 (TAPPI, 1980). Figure 19 presents visually the sheets of the unbleached and bleached pulps.

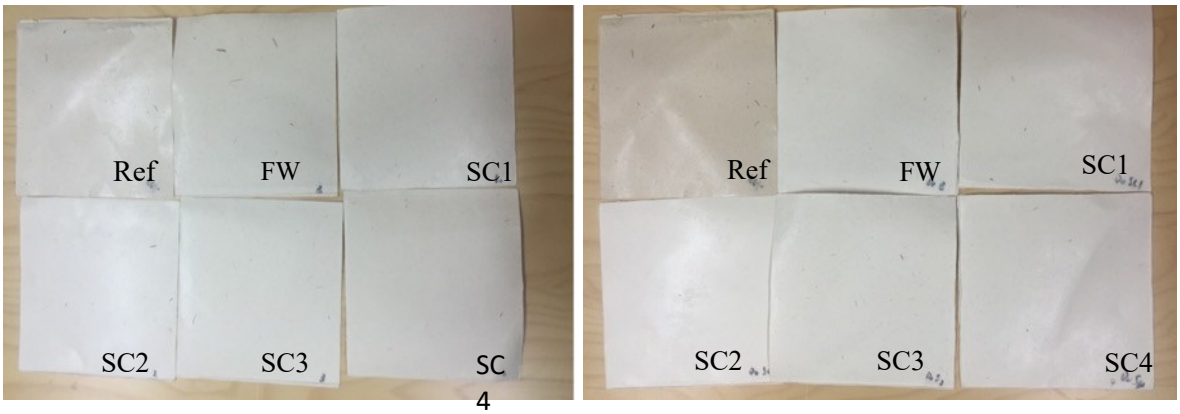


Figure 19. Hand sheets of unbleached and O_3 (Left) and D_0 (Right) bleached pulps. The use of fresh water or secondary condensates (SC1 to SC4) is shown in the photos

3.3.7.2. Kappa number

Kappa number of the pulps was measured based on the standard SCAN-C 1:00.

3.3.7.3. Viscosity

Pulp viscosity measurement was performed according to SCAN-CM 15:99.

3.3.7.4. ISO brightness

ISO brightness was measured with L&W SE 070R Elrepho spectrophotometer (Figure 20).

Figure 20. L&W SE 070R Elrepho spectrophotometer

4. RESULTS AND DISCUSSIONS

This chapter summarizes all the experimental results and their interpretation. Experimental raw data are presented in Appendix 1.

4.1. GC-MS Results

This section contains qualitative and quantitative results on the volatile components of secondary condensates, pulp filtrates and bleaching vapor phase.

Qualitative analysis of the chemical compounds is based on their mass spectra and retention times in gas chromatography, while quantification requires normalization of the signal intensity relative to a known added component, the internal standard (IS). Figure 21-25 represent the calibration curves for quantification of acetone, ethanol, DMDS, DMS and methanol relative to dibromomethane (IS). Most of the calibration curves were close to linear although there seemed to be quite significant experimental error in the measurements.

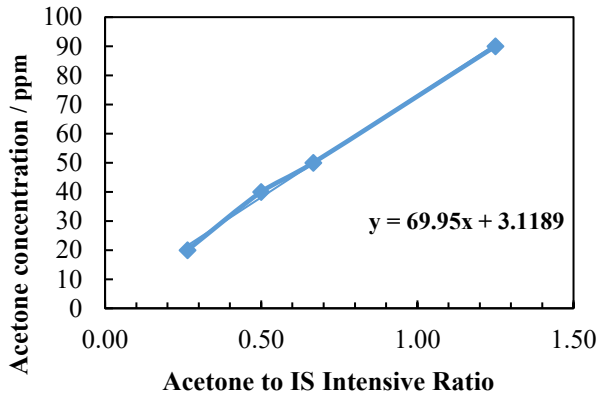


Figure 21. Calibration curve for quantification of acetone

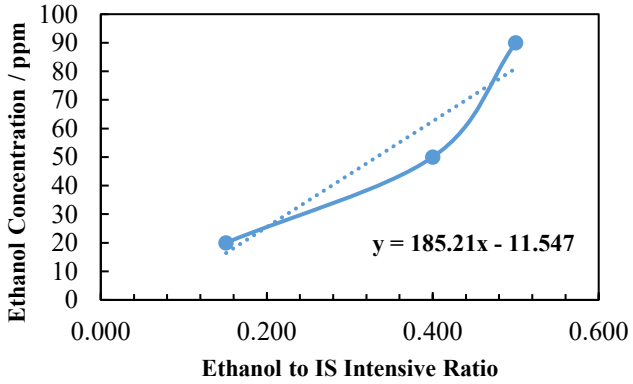


Figure 22. Calibration curve for quantification of ethanol

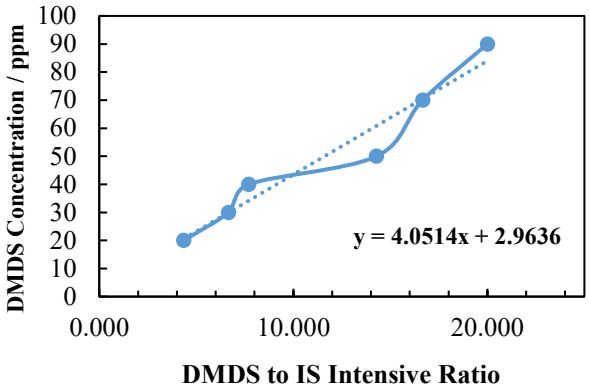


Figure 23. Calibration curve for quantification of DMDS

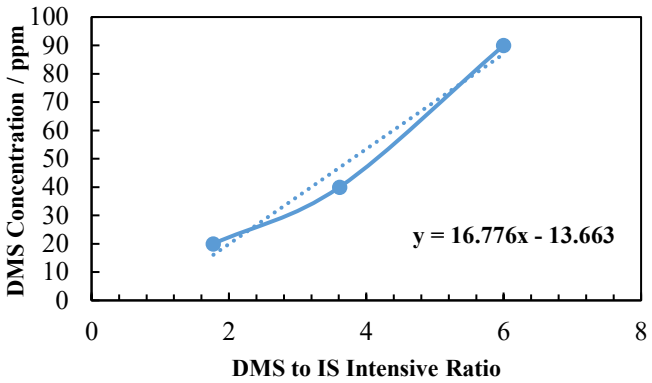


Figure 24. Calibration curve for quantification of DMS

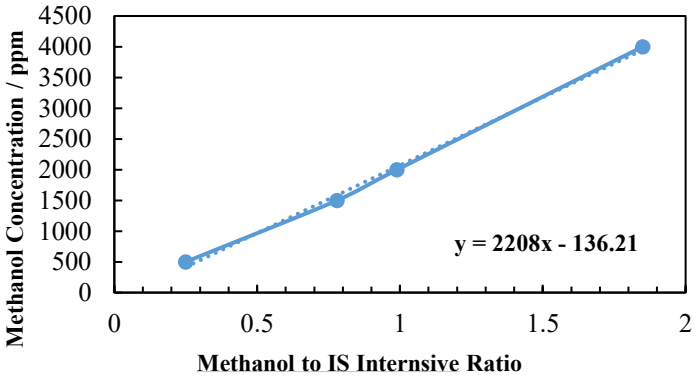


Figure 25. Calibration curve for quantification of methanol

4.1.1. Secondary Condensates

Table 8 presents qualitatively the identified components in the secondary condensates SC1-SC4. Figure 26 - Figure 31 show the corresponding chromatograms with total or selective ion detection by MS results of those four condensates. The identified components are listed in each case in the figure text. In many cases selective ion detection improved the resolution and enabled identification and quantification of certain components, such as methanol, that were otherwise impossible to detect.

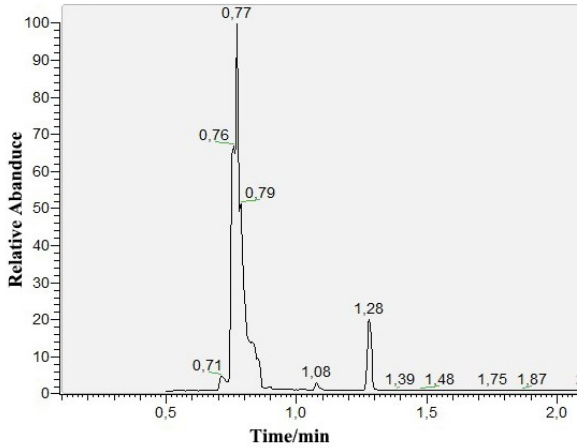


Figure 26. Head space gas chromatogram of SC1 (TIC). Identified components: acetone (1.08 min), IS (1.28 min).

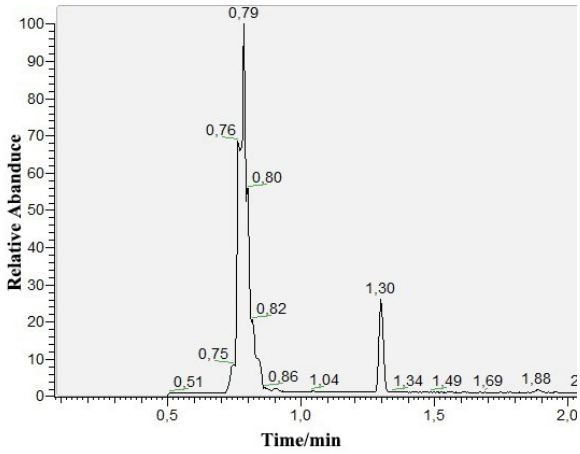


Figure 27. Head space gas chromatogram of SC2 (SIC). Identified components: methanol (0.82 min), IS (1.30 min).

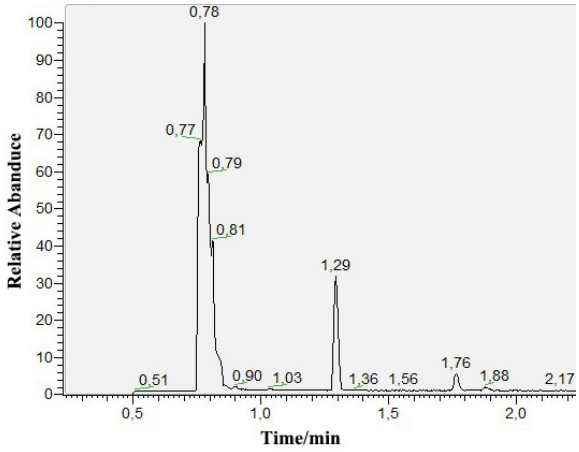


Figure 28. Head space gas chromatogram of SC3 (TIC). Identified components: IS (1.29 min).

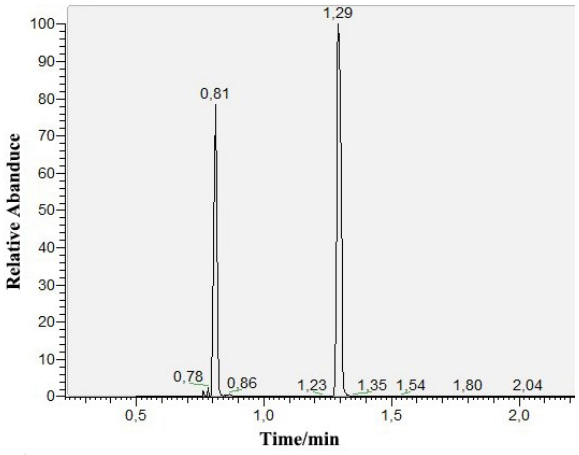


Figure 29. Head space gas chromatograms of SC3 (SIC). Identified components: methanol (0.81 min), IS (1.29 min).

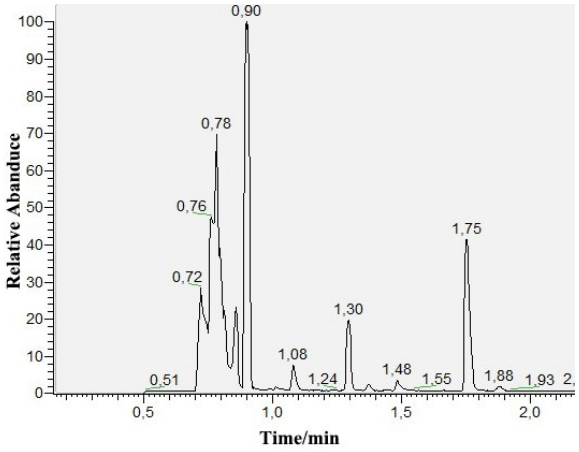


Figure 30. Head space gas chromatogram of SC4 (TIC). Identified components: 0.91 DMS (0.91 min), acetone (1.08 min), IS (1.30 min), DMDS (1.76 min).

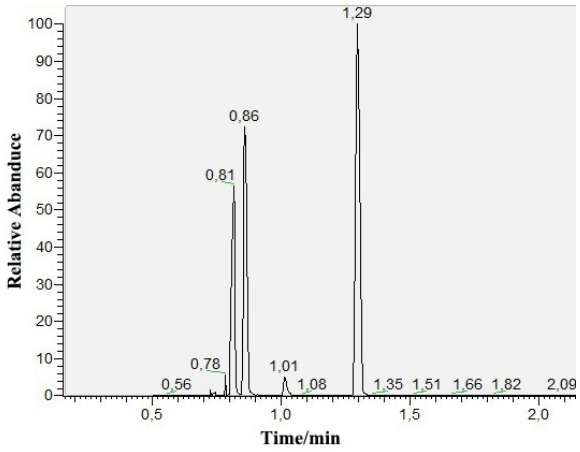


Figure 31. Head space gas chromatogram of SC4 (SIC). Identified components: methanol (0.81 min), ethanol (0.86 min), IS (1.29 min).

Table 8. Volatile compounds existed in secondary condensates identified by GC-MS

	Methanol	DMDS	DMS	Ethanol	Acetone
SC1					x
SC2	x				
SC3	x	x			
SC4	x	x	x	x	x

In a previous study, at least small amounts of methanol were found in all secondary condensates (Niemelä, 2000). In this work methanol was not identified in SC1, obviously due to the insensitivity of the method for very low methanol concentrations. Table 9 reports the concentrations of the identified components in each secondary condensate. Due to the relative large experimental error, the values are more approximate than accurate.

As showed in Table 9, SC4 was the "dirtiest" one among the four condensates since it contained relatively large amounts of all the impurities: methanol, ethanol, acetone, DMS and DMDS. Besides, SC4 had the strongest smell and it was not fully transparent (Figure 11). Large amounts of methanol were also present in SC3.

Table 9. Identified volatile component quantity in condensates

	Methanol / ppm	DMDS / ppm	DMS / ppm	Ethanol / ppm	Acetone / ppm
SC1	-	-	-	-	11
SC2	350	-	-	-	-
SC3	1300	3	-	-	-
SC4	900	8	11	160	25

4.1.2. Pulp Filtrates

Head space gas chromatograms of the bleaching filtrates are attached in Appendix 1. Table 10 and Table 11 summarize which volatile components were found in the bleaching filtrates and in which quantities. DMS and DMDS, that were present in SC3 and especially in SC4,

could not be detected at all in the bleaching filtrates. Obviously, the bleaching chemicals oxidized DMS and DMDS, probably to sulfate ion. Methanol was present in all filtrates, also when no secondary condensate was added as a diluent. Oxidation of lignin is known to result in its demethoxylation which explains the methanol formation during the bleaching stages (Wood, 1971, Ander, 1985, AnderKarl, 1985, Lopretti, 1998). Thus, methanol identified in the bleaching filtrates originate partly from the added condensates and partly from the oxidized lignin. Ethanol and acetone, that were present in SC4, existed also in the corresponding ozone bleaching filtrate. In contrast, acetone was not present in after adding SC4 to the chlorine dioxide bleaching stage. Thus, acetone was probably oxidized in this stage.

Table 10. Volatile component quantity in D0 pulp filtrates

	Methanol / ppm	DMDS / ppm	DMS/ ppm	Ethanol / ppm	Acetone / ppm
Fresh water	N.A.*	-	-	-	-
SC1	260	-	-	-	-
SC2	400	-	-	-	-
SC3	800	-	-	-	-
SC4	600	-	-	20	-

*Not identified

Table 11. Volatile component quantity in ozone pulp filtrates

	Methanol / ppm	DMDS / ppm	DMS / ppm	Ethanol / ppm	Acetone / ppm
Fresh water	130	-	-	-	-
SC1	140	-	-	-	-
SC2	320	-	-	-	-
SC3	800	-	-	-	-
SC4	600	-	-	40	15

4.1.3. Bleaching vapor phase

Head space gas chromatograms of vapor phase samples from the bleaching reactors are presented in Appendix 1. No volatile sulphur compounds were present in any of samples, thus confirming the oxidation of DMS and DMDS to non-volatile sulphur, probably sulfate ion. Methanol and ethanol were present in all the vapor samples.

4.1.4. Mass balance of methanol

The mass balance is made for bleaching process. From Section 4.1.1, the phenomena can be observed that there is certain amount of methanol exited in condensates. Thus, there are a few methanol contributions from condensates to filtrates. Table 12 presents methanol balance, in which list methanol formed during bleaching and from secondary condensates. Methanol content from secondary condensates is analyzed based on the added ratio of concentrate to the total bleaching volume (0.6l / 2l). Details illustration of calculation is presented in Appendix.

Table 12. Methanol balance of D_0 and Ozone bleaching by using different condensates

	Fresh water / ppm	SC1 / ppm	SC2 / ppm	SC3 / ppm	SC4 / ppm
Condensate	-	-	120	450	300
Formed in D_0 process	N.A.	260	280	350	500
Formed in O_3 process	130	140	200	350	300

Methanol formed during bleaching stage are not always keep in uniform. Reasons for this phenomenon could be that the un-uniform bleaching operation parameters, that lead to different methanol released by lignin methylation.

4.2. UV Raman spectra of bleached pulps

Figure 32 and Figure 33 show UV Raman spectra of the bleached pulps after their alkaline extraction. The Raman peak at 1605 cm^{-1} represents lignin, while the band at 1655 cm^{-1} originates from HexA. The spectra were normalized relative to the cellulose band intensity at ca. 1100 cm^{-1} and thus the y-axis intensity of the figures is proportional to the residual lignin and HexA contents in the pulps.

The use of the condensates seemed to have no clear effect on delignification and HexA removal in chlorine dioxide bleaching, even though there was some random variation between the experiments. In contrast, the dirtiness of the secondary condensates had possibly some effect on the residual lignin and HexA contents in ozone bleaching.

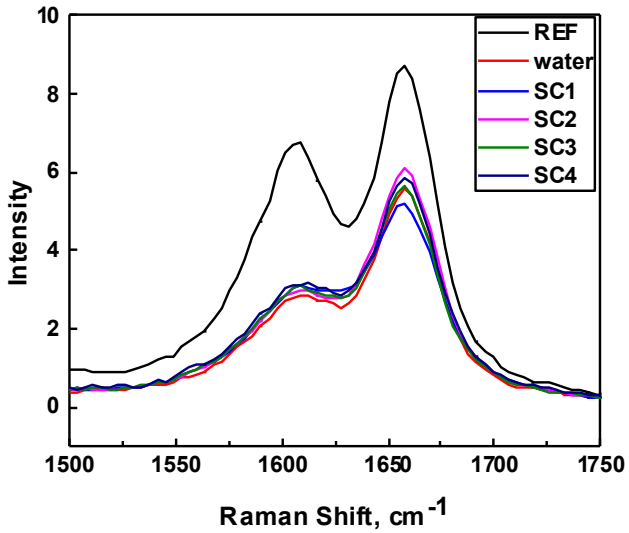


Figure 32. Effect of secondary condensates on UV Raman spectra of D_0 bleached pulps

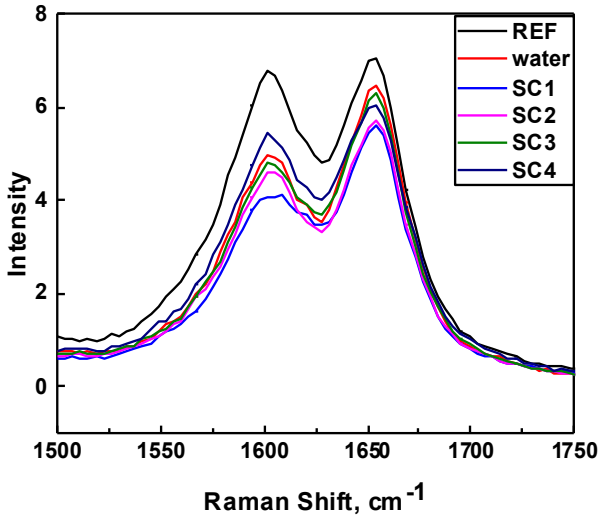


Figure 33. Effect of secondary condensates on UV Raman spectra of O_3 bleached pulps

4.3. Total Sulphur Content

Figure 34 illustrates total sulphur content in SC3, SC4, and the D_0 filtrates from trials where fresh water, SC3, and SC4 were used as diluents. It is clearly evident that most of the sulphur in the filtrates originated from the pulp while even the dirtiest of all the condensates, SC4, contributed little to the total sulphur content. On the other hand, the total sulphur content of SC4 was high in comparison with its DMS and DMDS contents (Table 9).

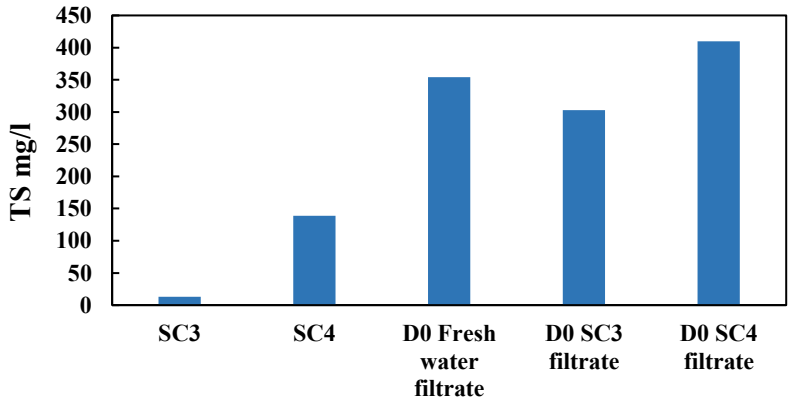


Figure 34.Total sulphur content in SC3, SC4, fresh water D_0 filtrate, SC3 D_0 filtrate, SC4 D_0 filtrate.

The reason for the high sulphur content of the pulp could be the incomplete washing after the kraft cooking and oxygen delignification or covalent bonding of sulphur on the pulp.

4.4. COD

This chapter summarizes COD levels of all condensates and pulp filtrates, and the analysis of COD mass balance. In another hand, this chapter analyzes the environmental load of utilizing secondary condensates in bleaching.

4.4.1. COD of Condensates and Filtrates

COD levels of the secondary condensates and the bleaching filtrates are presented in Table 13. The contribution of the use each condensate on the filtrate COD can be estimated my multiplying the SC COD value with the dilution ratio (0.6/2).

Table 13. COD levels (mg/l) of secondary condensates and bleaching filtrates

	O_3 filtrate	D_0 filtrate	Secondary condensate
Fresh Water	1131	2244	
SC1	989	1600	250
SC2	1238	1501	387
SC3	1550	2135	1059
SC4	2832	3601	3296

SC4 shows the highest COD value. The insoluble of the upper phase of SC4 is one possible origin of the high COD besides methanol, DMS, DMMS, etc. The water insoluble fraction of SC4 might contain e.g. some terpenes, that could lead to additional COD load. Section 4.4.2 demonstrates the COD balance of filtrates.

4.4.2. COD Balance of Bleaching

Besides the secondary condensates, solubilization of oxidized of lignin and HexA contributed to the filtrate COD. However, there are also other 'unknown' sources of COD (Figure 35). These possible sources include at least some carbohydrate yield losses.

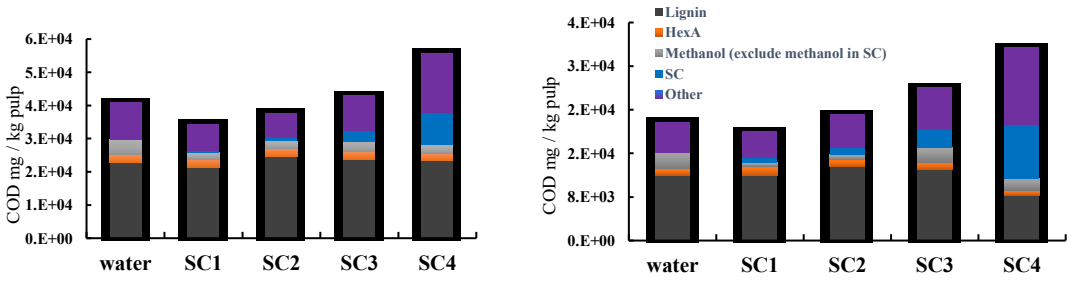


Figure 35.COD mass balance of D_0 (Left) and O_3 (Right) bleaching by utilizing secondary condensates (SC is excluded methanol in this figure)

4.5. Pulp Properties

4.5.1. Kappa number

D_0 bleaching of the birch kraft pulp reduced its kappa number from 15 to 6.5-8. Although not using a secondary condensate led to the lowest kappa number, the type of the secondary condensate used as a diluent seemed to have no effect. The kappa number drop was much smaller in O_3 bleaching, only 1.5-3 kappa number units. The use of the dirtiest condensate, SC4, resulted in the highest residual kappa number. However, the effect of the dirtiness of the secondary condensates was not completely obvious because not using a secondary condensate led also to a marginal kappa number drop. Interestingly, the kappa number measurement and UV Raman spectroscopy ranked the pulps similarly.

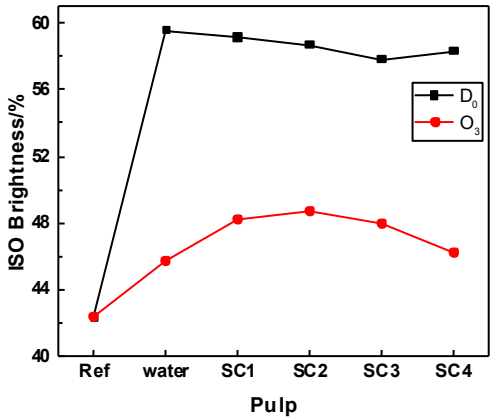


Figure 36. ISO brightness of birch kraft pulp bleached by D_0 and O_3 in the absence and presence of secondary condensates.

4.5.2. ISO Brightness

ISO brightness values of D_0 and O_3 bleached pulp are presented in Figure 36. D_0 bleaching increased the brightness from the original 42 % to 58-60 %. The dirtiness of the secondary condensates used as diluents had barely any effect on the brightness. O_3 bleaching increased the brightness only to the level of 46-48.5 %. Irrespective of the way of bleaching, the brightness correlated linearly with kappa number. Thus, the brightness depended mostly on the residual lignin content that was obviously more affected by random variation in the bleaching experiments rather than the use of the secondary condensates. However, the effect of condensates on brightness was possibly slightly negative in this study, similar to previous research (Niemelä, 2000, Sankari, 2004).

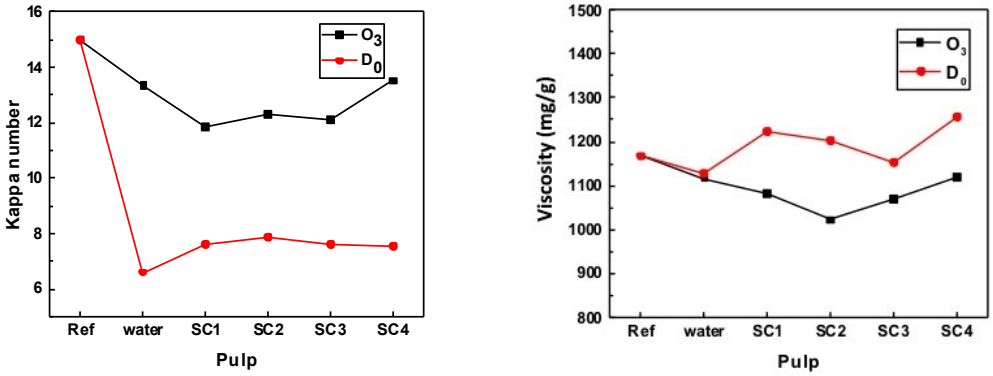


Figure 37. Kappa number (left) and viscosity (right) of birch kraft pulp bleached by D_0 and O_3 in the absence and presence of secondary condensates

4.5.3. Viscosity

Figure 37 presents the variation in pulp viscosity between the bleaching experiments. Ozone bleaching decreased the viscosity by ca. 100 units (ml/g) in comparison with chlorine dioxide bleaching. However, the possible effects of the use of the secondary condensates was within experimental variation.

5. CONCLUSIONS AND SUGGESTIONS FOR FURTHER STUDIES

Four secondary condensates from black liquor evaporation plant were characterized and applied for laboratory bleaching of a birch kraft pulp as a partial replacement of fresh water. The main volatile components of the secondary condensates were methanol, acetone, ethanol, dimethyl sulfide (DMS) and dimethyl disulfide (DMDS). All the mentioned compounds were present in SC4, the "dirtiest" one among the condensates. In contrast, only acetone was identified in SC1. SC3 had the highest methanol content whereas SC4 had the highest COD. SC4 differed from the other condensates through separation of a turbid liquid phase on the top of the storage flask. This fraction possibly contained terpenes that were responsible for the high COD.

No volatile sulphur compounds were identified in the bleaching filtrates or the vapor phase. The bleaching chemicals, chlorine dioxide and ozone, probably oxidized DMS and DMDS to sulfate. Moreover, the added secondary condensates contributed only little to the total sulphur content of the bleaching filtrates in comparison with the carryover from the pulp. In contrast, the dirtiest filtrates contributed significantly to COD and methanol content of the bleaching filtrates. The bleaching result, characterized by brightness, kappa number and UV Raman spectroscopy, was only slightly if not at all affected by the condensate use. These results confirm that secondary condensates can be safely utilized in pulp bleaching to eliminate fresh water consumption.

The present study did not allow building detailed mass and COD balances of the bleaching stages when fresh water was partially replaced with secondary condensates. A detailed understanding on the reactions occurring during pulp bleaching would be required to construct more accurate COD and methanol mass balances. For example, the mechanism, kinetics and stoichiometry of methanol formation should be studied quantitatively as the function of lignin conversion and removal.

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APPENDICES

APPENDIX 1. Raw data on quantification of VOC components by head space GC-MS
APPENDIX 2. Quantification of lignin and Hexenuronic acid reduction based on UV-Raman and illustration of COD mass balance
APPENDIX 3. Raw data of total sulphur content
APPENDIX 4. Raw data of pulp properties

APPENDIX 1. Raw data on quantification of VOC components by head space GC-MS

1.1. Calibration data for quantification of VOC components

Table 14-18 present the dependences between the concentration of individual VOC components and their GC-MS intensity ratio relative to the internal standard (dibromomethane) under conditions described in the experimental.

Table 14. Relative intensity ratio of methanol vs. its concentration

Intensity ratio	Concentration/ppm
0.25	500
0.78	1500
0.99	2000
1.85	4000

Table 15. Relative intensity ratio of DMS vs. its concentration

Intensity Ratio	Concentration/ppm
1.77	20
3.61	40
6.00	90

Table 16. Relative intensity ratio of acetone vs. its concentration

Intensity Ratio	Concentration/ppm
0.26	20
0.50	40
0.67	50
1.25	90

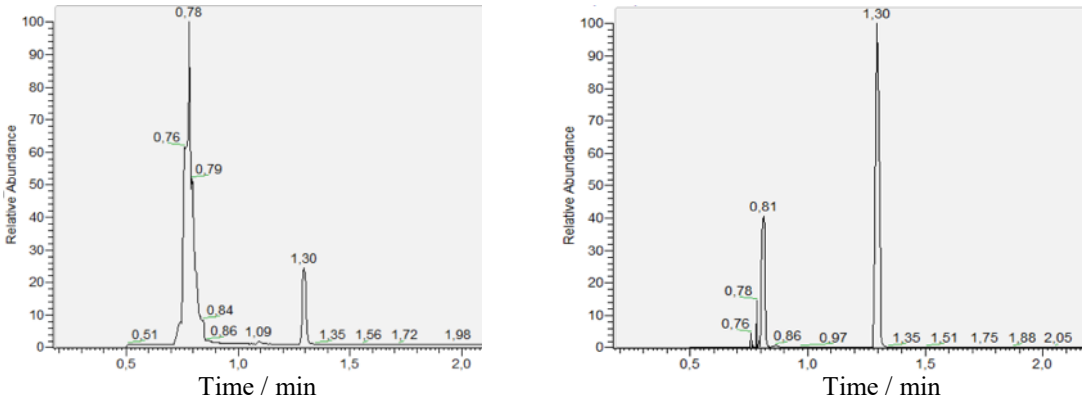
Table 17. Relative intensity ratio of ethanol vs. its concentration

Intensity Ratio	Concentration/ppm
0.15	20
0.40	50
0.50	90

Table 18. Relative intensity ratio of DMDS vs. its concentration

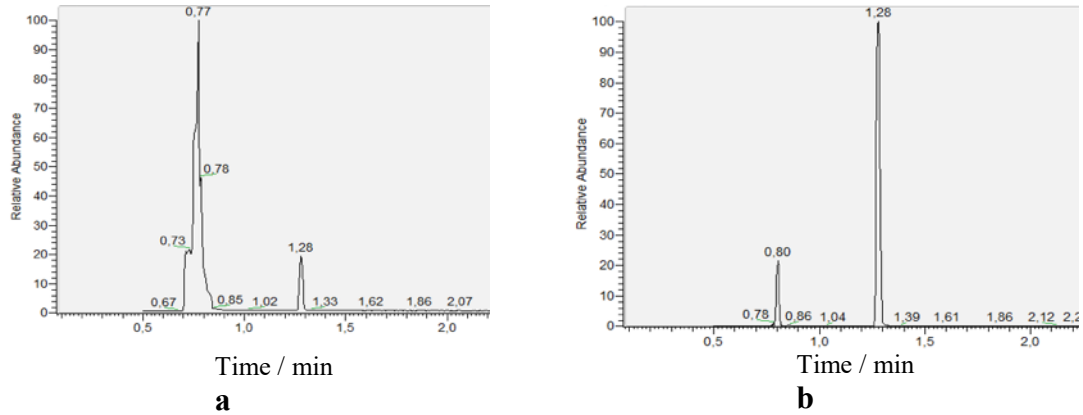
Intensity ratio	Concentration/ppm
4.35	20
6.67	30
7.69	40
14.29	50
16.67	70
20.00	90

1.2. Head space gas chromatograms of bleaching filtrates



a **b**

Figure 38. D_0 stage filtrate without SC addition. a) TIC, b) SIC; methanol (0.81 min), IS (1.30 min)



a **b**

Figure 39. D_0 stage filtrate with SC1 addition. a) TIC, b) SIC; methanol (0.80 min), IS (1.28 min)

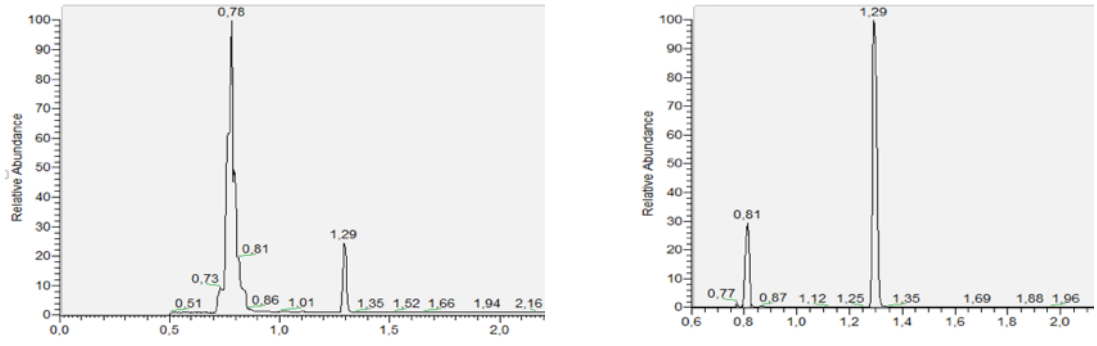


Figure 40. D_0 stage filtrate with SC2 addition. a) TIC, b) SIC; methanol (0.81 min), IS (1.29 min)

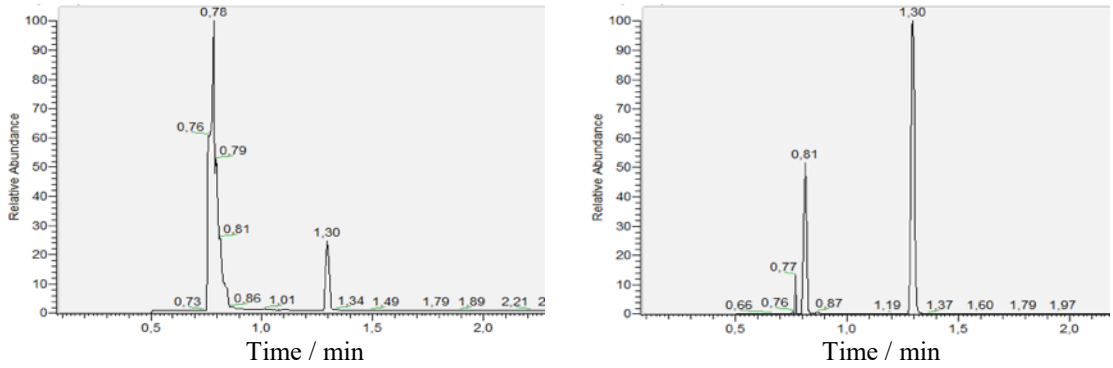


Figure 41. D_0 stage filtrate with SC3 addition. a) TIC, b) SIC; methanol (0.81 min), IS (1.30 min)

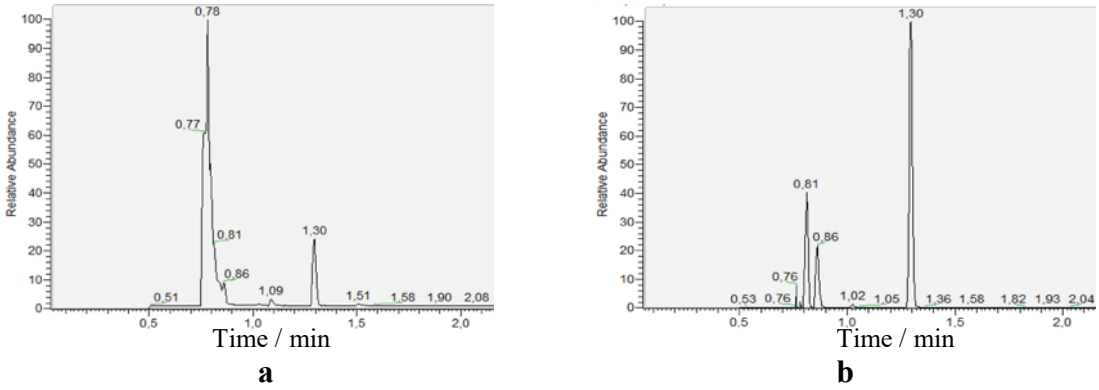


Figure 42. D_0 stage filtrate with SC4 addition. a) TIC, b) SIC; methanol (0.80 min), ethanol (0.86 min), acetone (1.09 min), IS (1.28 min)

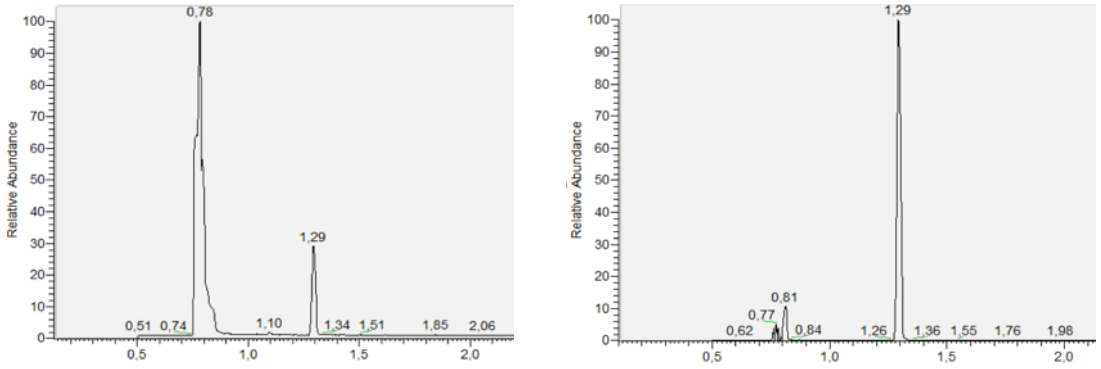


Figure 43. Z stage filtrate without SC addition. a) TIC, b) SIC; methanol (0.81 min), acetone (1.10 min), IS (1.29 min)

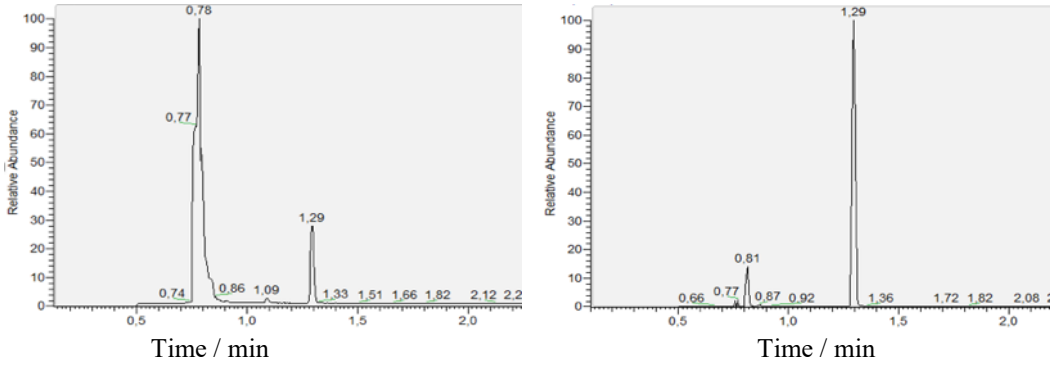


Figure 44. Z stage filtrate with SC1 addition. a) TIC, b) SIC; methanol (0.81 min), acetone (1.09 min), IS (1.29 min)

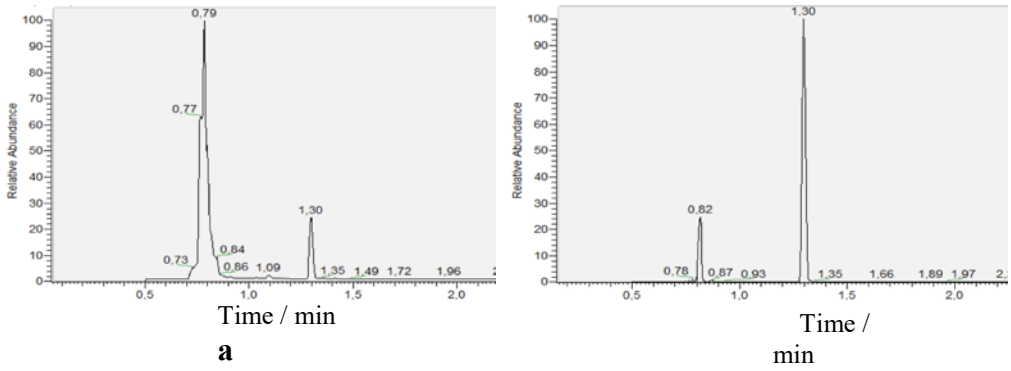


Figure 45. Z stage filtrate with SC2 addition. a) TIC, b) SIC; methanol (0.82 min), acetone (1.09 min), IS (1.30 min)

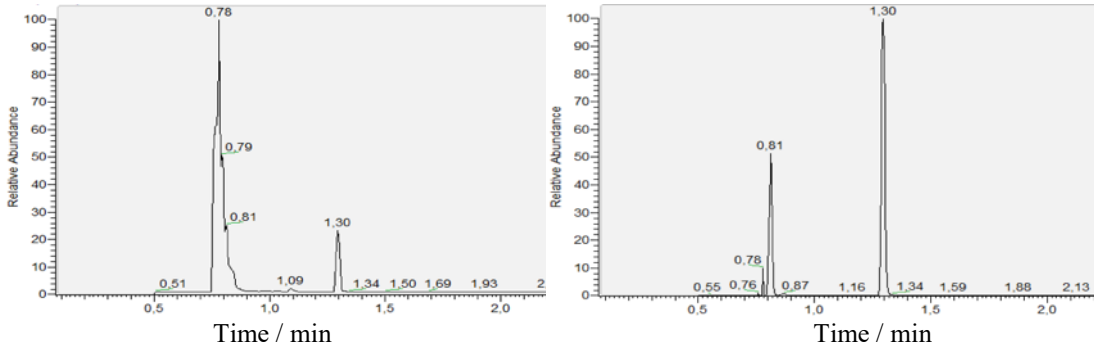


Figure 46. Z stage filtrate with SC3 addition. a) TIC, b) SIC; methanol (0.81 min), acetone (1.09 min), IS (1.30 min)

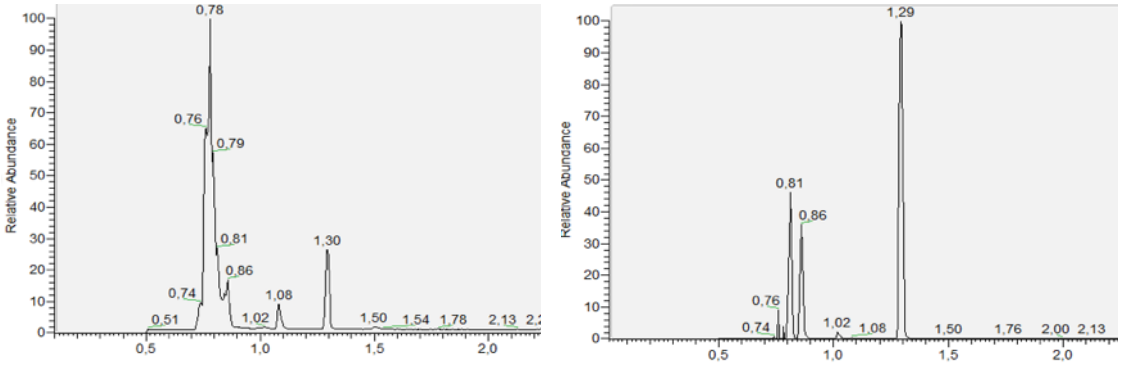


Figure 47. Z stage filtrate with SC4 addition. a) TIC, b) SIC; methanol (0.81 min), ethanol (0.86 min), acetone (1.08 min), IS (1.29 min)

1.3. Head Space Gas Chromatograms of Bleaching Vapor Phase Samples

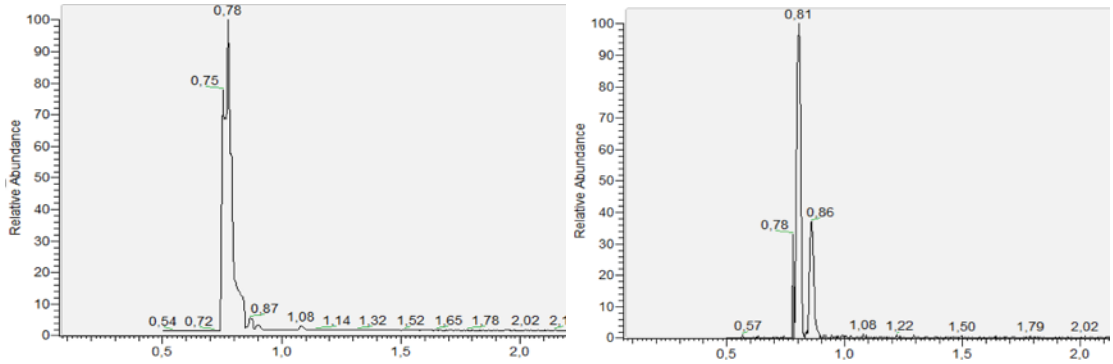


Figure 48. D_0 bleaching stage without SC addition. a) TIC, b) SIC; methanol (0.81 min), ethanol (0.86 min), acetone (1.08 min).

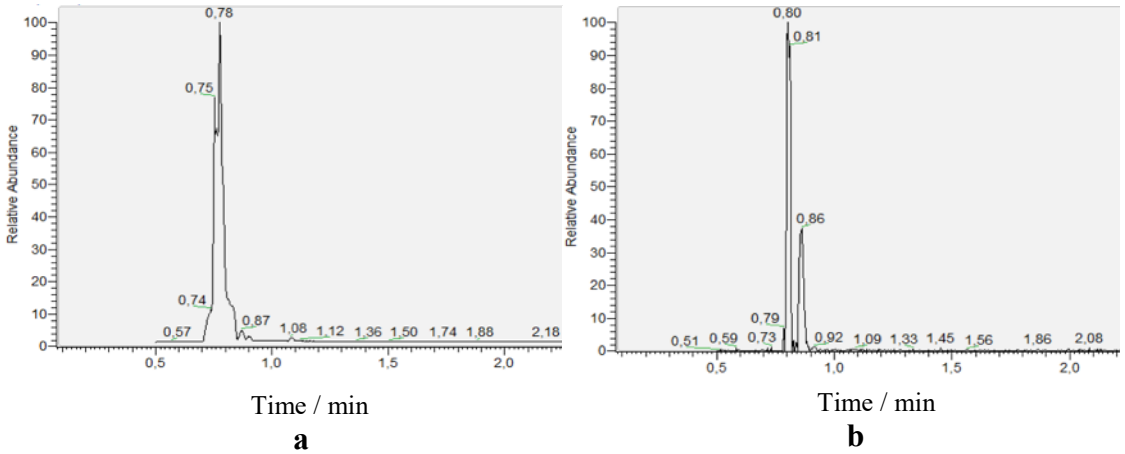


Figure 49. D_0 bleaching stage with SC1 addition. a) TIC, b) SIC; methanol (0.81 min), ethanol (0.86 min), acetone (1.08 min).

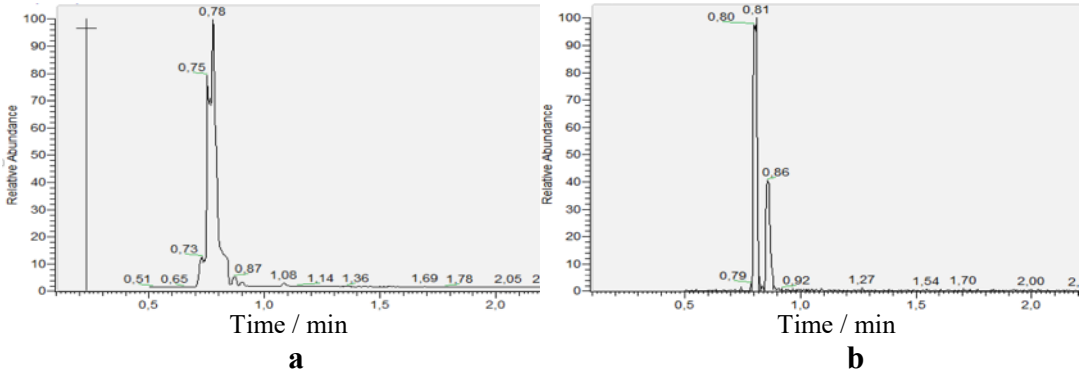


Figure 50. D_0 bleaching stage with SC2 addition. a) TIC, b) SIC; methanol (0.81 min), ethanol (0.86 min), acetone (1.08 min).

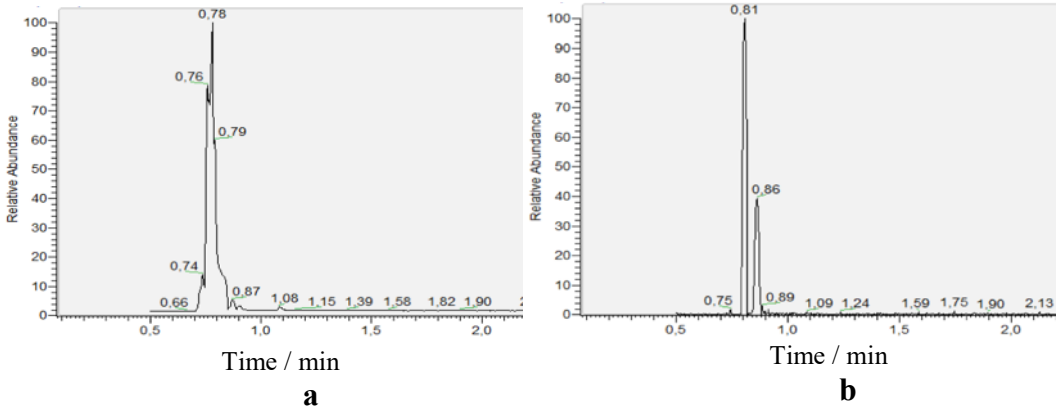


Figure 51. D_0 bleaching stage with SC3 addition. a) TIC, b) SIC; methanol (0.81 min), ethanol (0.86 min), acetone (1.08 min).

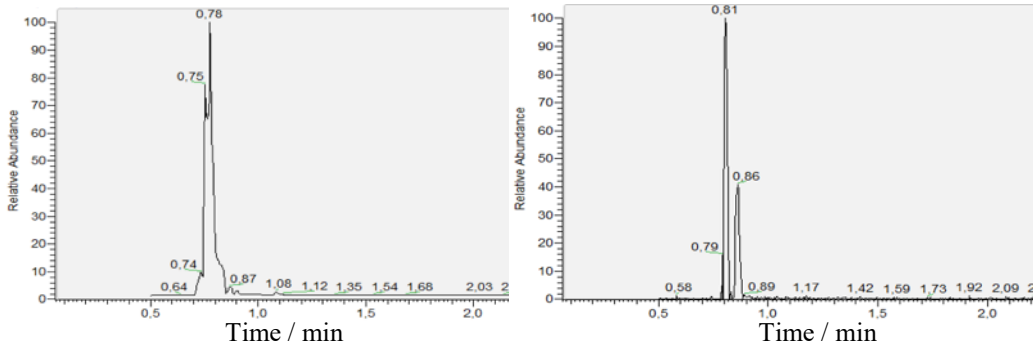


Figure 52. D_0 bleaching stage with SC4 addition. a) TIC, b) SIC; methanol (0.81 min), ethanol (0.86 min), acetone (1.08 min).

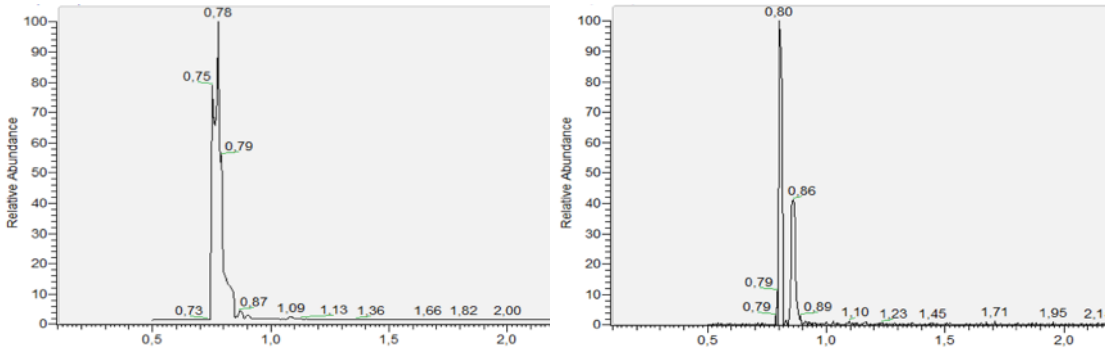


Figure 53. Z bleaching stage without SC addition. a) TIC, b) SIC; methanol (0.81 min), ethanol (0.86 min).

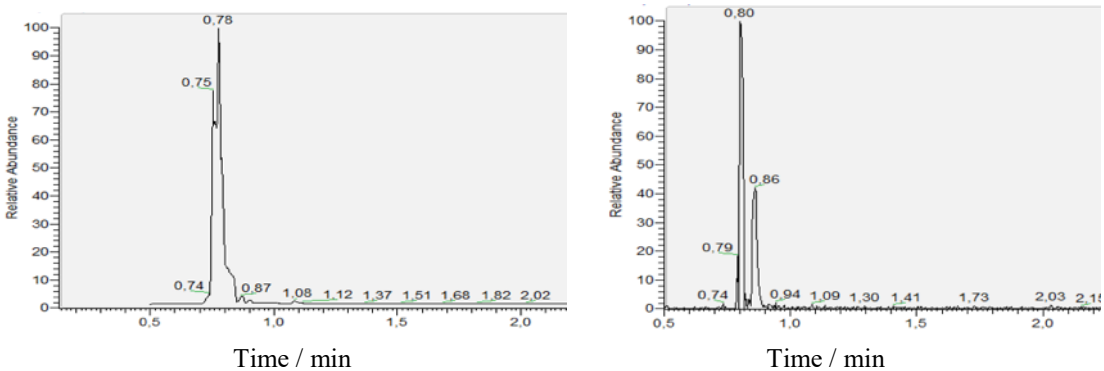


Figure 54. Z bleaching stage with SC1 addition. a) TIC, b) SIC; methanol (0.81 min), ethanol (0.86 min), acetone (1.08 min).

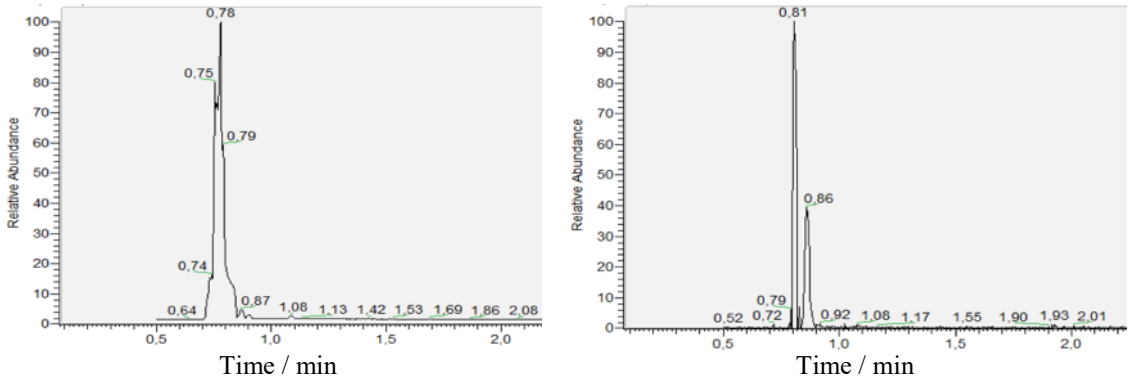


Figure 55. Z bleaching stage with SC2 addition. a) TIC, b) SIC; methanol (0.81 min), ethanol (0.86 min), acetone (1.08 min).

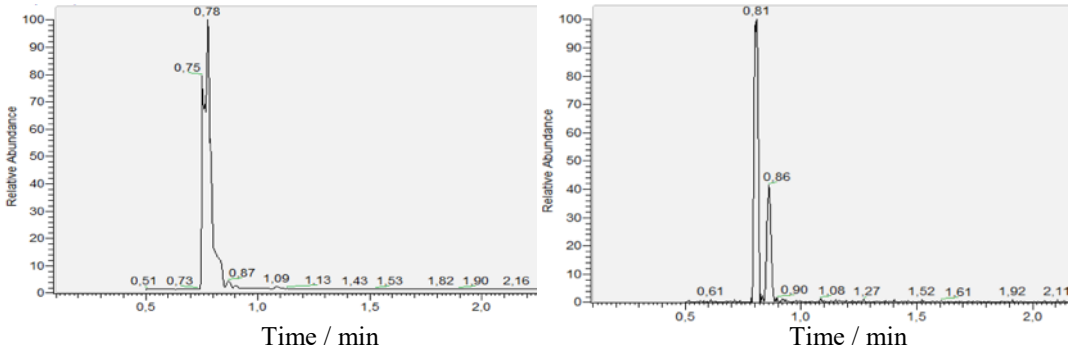


Figure 56. Z bleaching stage with SC3 addition. a) TIC, b) SIC; methanol (0.81 min), ethanol (0.86 min), acetone (1.09 min).

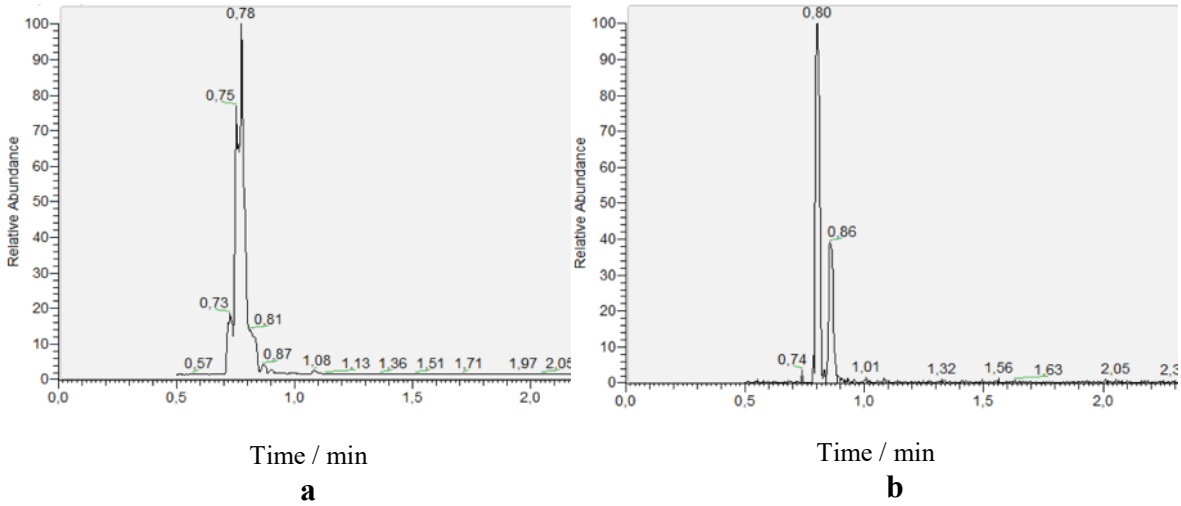


Figure 57. Z bleaching stage with SC4 addition. a) TIC, b) SIC; methanol (0.80 min), ethanol (0.86 min), acetone (1.08 min).

APPENDIX 2. Quantification of lignin and Hexenuronic acid reduction based on UV-Raman and illustration of COD mass balance

During bleachinsg operations, delignification and other chemical reactions happened. And reduction of lignin and HexA can lead to kappa number decreasing. To construct the overall and COD mass balance, lignin and HexA reduction during O_3 and D_0 bleaching operations were quantified. Calculation procedures and details illustrations are listed below.

The decreased lignin and HexA amount in bleaching process is calculated based on UV-Raman spectroscopy. The quantity of lignin and HexA from UV-Raman spectroscopy got by follow equations (Jääskeläinen, 2005).

Equation 1 is for lignin content in pulp calculation based on UV-Rama spectra, while equation 2 is for HexA.

Equation 1: $\text{Lignin (\%)} = 0.32 * \frac{\text{I(1065 cm}-1)}{\text{I(1094 cm}-1)}$

Equation 2: $\text{HexA (mmol/kg)} = 4.39 * \frac{\text{I(1655 cm}-1)}{\text{I(1094 cm}-1)} - 1.14$

Table 19 and Table 20 present lignin and HexA content in D_0 bleached and ozone bleached pulp. By comparing those two compounds content in bleached pulp with those in reference pulp, the decreased lignin and HexA content are obtained and listed in Table 21 and Table 22.

Table 19.Lignin content and HexA content in D_0 bleached pulp

	Ref	water	SC1	SC2	SC3	SC4
Lig cont %	2.144	0.89	0.968	0.932	0.972	0.996
HexA cont / mmol/kg	28.267	11.069	12.143	11.648	12.197	12.549

Table 20.Lignin content and HexA content in O_3 bleached pulp

	Ref	water	SC1	SC2	SC3	SC4
Lig cont %	2.144	1.597	1.504	1.521	1.544	1.777
HexA cont / mmol/kg	28.5232	20.47	16.73	19.62	19.88	22.51

Table 21. Removed lignin and HexA content after D_0 stage.

	water	SC1	SC2	SC3	SC4
Lig cont %	1.254	1.176	1.212	1.172	1.148
HexA / mmol/kg	17.198	16.12	16.62	16.07	15.72

Table 22.Removed lignin and HexA content after O_3 stage.

	water	SC1	SC2	SC3	SC4
Lig cont / %	0.592	0,640	0.668	0.645	0.412

HexA cont / mmol/kg	8.05	11,73	8.9	8.64	6.02

As an example, the COD contribution given by decreased lignin and HexA in SC1 D_0 bleached pulp will be illustrated here.

Decreased lignin and HexA amount of D_0 bleached pulp in Table 21 is described in unit "% wt" of pulp and "mmol/kg pulp" respectively. To calculate the COD contribution, those value need to be present in unit of mol or mmol. The total volume of bleaching operation is 2 L including pulp and used pulp is 200g odt.

The chemical element composition of birch lignin is $C_9H_{7.89}O_{2.53}(OCH_3)_{1.39,}$ thus it molar weight is 199.06 (Pettersen, 1984).

Mass weight of decreased lignin of SC1 bleached D0 pulp: 1.176% * 200g= 2.49g
Molar weight of decreased lignin of SC1 bleached D0 pulp: (2.49g * 1000)/ 199.06 = 13 mmol

The COD calculation is made based on the chemical reaction below.

$$\mathrm{CnHaObNc} + \left(\frac{n+a}{4} + \frac{b}{2} - \frac{3}{4c}\right)\mathrm{O2} \rightarrow \mathrm{nCO2} + \left(\frac{a}{2} - \frac{3}{2c}\right)\mathrm{H2O} + \mathrm{cNH}$$

$\frac{n+a}{4} + \frac{b}{2} - \frac{3}{4c} = 11.345$. Since lignin molar weight is 13 mmol, O_2 consumption of oxidase lignin is 13 mmol *1000*11.345*32 g/mol =4290 mg. Thus the COD contribution of SC1 bleached D_0 stage pulp is 4290 mg.

Then HexA COD contribution is explained below. There are 16.12 mmol/kg pulp is removed during bleaching, which means 16.12 mmol/kg * 0.2 kg = 3.22 mmol HexA is removed. The chemical composition of HexA is $C_6H_8O_7$ and n+a/4-b/2 -3/4c= 4.5. Thus, the COD contribution given by removed HexA is 3.22 mmol *1000* 4.5 *32 g/mol = 464 mg/l.

The COD contribution given by reacted lignin and HexA in condensate and water bleaching process are presented in Table 23 and Table 24.

Table 23. COD contribution given by removed lignin

	water	SC1	SC2	SC3	SC4
D0 / mg/l	4541	4290	4916	4754	4657
O3 / mg/l	2401	2385	2710	2616	1671

Table 24. COD contribution given by removed HexA

	water	SC1	SC2	SC3	SC4
D0 / mg/l	495	464	479	463	453
O3 / mg/l	232	338	256	249	173

To construct COD mass balance, methanol in filtrates is an important part in COD consistence. The method for methanol COD calculation is similar to HexA and lignin COD calculation method. Table 25 and Table 26 display COD composition of D_0 and Z bleached filtrates from different sources.

Table 25. COD Composition of D_0 Bleached Pulp Filtrates

	Lignin	HexA	Methanol (exclude methanol in SC)	SC	Other
water-bleached-filtrate COD	22706	2474	1950		11220
SC1-bleached-filtrate COD	21448	2321	1950	375	7999
SC2-bleached-filtrate COD	24581	2393	2212.5	581	7503
SC3-bleached-filtrate COD	23770	2314	3075	1588	10674
SC4-bleached-filtrate COD	23283	2264	2475	4944	18005

Table 26. COD Composition of Z Bleached Pulp Filtrates

	Lignin	HexA	Methanol (exclude methanol in SC)	SC	Other
water-bleached-filtrate COD	12007	1159	650		5655
SC1-bleached-filtrate COD	11926	1689	700	375	4945
SC2-bleached-filtrate COD	13548	1282	1000	581	6190
SC3-bleached-filtrate COD	13082	1244	2800	1588	7750
SC4-bleached-filtrate COD	8356	867	2100	4944	14160

APPENDIX 3. Raw data of total sulphur content

The total sulphur content of part of condensates and filtrates is displayed in this section (Table 27).

Table 27. Total sulphur content of condensates and filtrates.

Sample ID	SC3	SC4	SC3 D0 filtrate	SC4 D0 filtrate	Fresh water D0 filtrate
Total sulphur / mg/l	13.1	139	303	410	354

APPENDIX 4. Raw data of pulp properties

4.1. ISO Brightness

Table 28 presents the ISO Brightness of pulps bleached by condensates and comparison with reference pulp.

Table 28. ISO Brightness of D_0 and O_3 bleached pulp by different condensates

	D0 ISO brightness / %	O3 ISO brightness / %
Ref	42.31	42.31
Fresh water	59.57	45.72
SC1	59.15	48.17
SC2	58.70	48.76
SC3	57.83	47.95
SC4	58.32	46.16

4.2. Kappa number

Table 29 presents the Kappa number of pulps bleached by condensates and comparison with reference pulp.

Table 29. Kappa number of D_0 and O_3 bleached pulp by different condensates

	Ref	water	SC1	SC2	SC3	SC4
D0	15	6.6	7.6	7.8	7.6	7.5
O3		13.3	11.9	12.3	12.1	13.5

4.3. Viscosity

Table 30 presents v iscosity of D_0 and O_3 bleached pulp by different condensates and comparison with reference pulp.

Table 30. Viscosity of D_0 and O_3 bleached pulp by different condensates

	O3 viscosity / mg/l	D0 viscosity / mg/l
Reference	1167	
Fresh water	1117	1127
SC1	1081	1222
SC2	1023	1202
SC3	1069	1153
SC4	1120	1256

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